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16. ABSTRACT The report gives results of a search of U.S. literature to identify published information about trace metals and Stationary Conventional Combustion Processes (SCCPs). The search was initially computerized with later cross referencing from identified reports. The report summarizes the information found in the literature and includes specific references. It summarizes what has been published about ambient trace metals in air, water, and soils. A survey, reporting the trace metal concentration in combustible fuels, identifies coal as the fuel of most concern; generally, trace metal levels in coal are similar to their crustal abundances. It reviews conventional combustion technology. It discusses trace metal flows and partitioning around various types of boilers and pollution control devices, and reports data from cited studies. In addition to coal, the report gives data for oil, municipal refuse, and wood. It also covers emissions to air, water, and soil, including trace metal leaching. It documents the health and environmental effects of trace metals. Where possible, it assesses specific contributions from SCCPs. It covers environmental transport systems, as well as special problems associated with radioactive metals and SCCPs.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
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Trace Elements	Wastes	Stationary Sources	06A	14G
Radioactive Materials	Wood	Trace Metals	18H	11L
Combustion Products	Leaching	Municipal Refuse	21B	07D, 07A
Coal			21D	
Boilers			13A	

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TRACE METALS AND STATIONARY CONVENTIONAL COMBUSTION SOURCES

Volume 1

Technical Report

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ABSTRACT

This is the principal volume of a two-volume report that gives results of a search of U.S. literature to identify published information about trace metals and Stationary Conventional Combustion Processes (SCCPs). The search was initially computerized with later cross referencing from identified reports. The report summarizes the information found in the literature and includes specific references. It summarizes what has been published about ambient trace metals in air, water, and soils. A survey, reporting the trace metal concentration in combustible fuels, identifies coal as the fuel of most concern; generally, trace metal levels in coal are similar to their crustal abundances. It reviews conventional combustion technology. It discusses trace metal flows and partitioning around various types of boilers and pollution control devices, and reports data from cited studies. In addition to coal, the report gives data for oil, municipal refuse, and wood. It also covers emissions to air, water, and soil, including trace metal leaching. It documents the health and environmental effects of trace metals. Where possible, it assesses specific contributions from SCCPs. It covers environmental transport systems, as well as special problems associated with radioactive metals and SCCPs.

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SECTION 1

INTRODUCTION

The role that trace metals play in the environment has been a subject of increasing interest. Three factors have combined to provide much of the impetus behind this growing concern:

- Increasing energy demands are being met by the increasing use of fossil fuels, particularly coal. Coal contains essentially all the trace metals in roughly the same abundance as in the earth's crust. Massive burning of coal has become a major anthropogenic mobilization pathway by which these trace metals enter the biosphere.
- Improved analytical technology in the 1970's has provided a higher quality and quantity of data on trace metals. Only with these improved data can the impact of trace metal emissions be assessed. Indeed, many effects of trace metals in the environment are yet to be identified.
- There is a growing awareness and concern about environmental factors influencing health. More and more, statistical studies are implying a relationship between diseases and factors in the environment such as trace metals.

To meet the need for a comprehensive assessment of the environmental effects of stationary conventional combustion processes, the Environmental Protection Agency's Industrial Environmental Research Laboratory at Research Triangle Park (EPA/IERL-RTP), N.C., established a Conventional Combustion Environmental Assessment (CCEA) program in February 1977. This CCEA program was chartered to assess comprehensively the effects of pollutants released from conventional combustion processes and associated control technologies on human health, the ecology, and the general environment, and to recommend measures for controlling adverse effects to within acceptable limits. The program concentrates upon Stationary Conventional Combustion Processes (SCCP) in the utility, industrial, residential, and commercial use sectors.

In 1977 IERL-RTP initiated the CCEA program. Initially Kenkeremath *et al*. (1) wrote a report to assist in the implementation of the program and Thompson and Harrison (2) published a survey of projects supported or conducted by EPA relevant to the CCEA program, including current research as of July 1978. These studies reported that some data already existed, although dispersed and of uneven quality. They recommended an information search to establish a database needed to implement the CCEA program. In 1978, EPA contracted with Radian Corporation to bring together all relevant information on trace metals that are emitted from stationary conventional combustion processes/equipment and produce a detailed summary environmental assessment report. In addition to this main report, which will establish the information database, a short technical summary and a separate bibliography have also been published.

1.1 DEFINITIONS

The exact definition that was used in this study for an SCCP (Stationary Conventional Combustion Process) was taken from Thompson and Harrison (2) and consultations with the project officer. The sources specifically considered were:

- utility boilers (coal, oil, gas),
- packaged boilers,
- residential heaters,
- refuse and wood boilers, and
- turbines.

The majority of the literature on trace metals and fuels or emissions concerns coal, and the number of pages devoted to coal in this report reflects that proportion. Almost nothing was found relating to residential heating and turbines. The details of the literature search are given in Section 1.2.

Types of sources specifically not covered under the SCCP definition were:

- fluidized-bed combustion,
- coal gasification or liquefaction,
- oil shale retorting,

- industrial process heating,
- refineries,
- mobile combustion sources, and
- nuclear.

In certain sections, reference to or comparison with some of these types of processes has been made, but in general, they have not been considered.

The directive for this work specified that trace metals only were to be considered. However, most researchers, in performing trace analysis, report many elements including the trace metals. Trace elements are often defined as elements whose concentrations are less than 100 ppm. But some concentrations vary widely, and no precise definition is possible. Frequently used classifications from a variety of environmentalists and chemists appear in Table 1-1.

TABLE 1-1. CLASSICAL DEFINITIONS OF NON-TRACE METAL ELEMENTS

Minor Elements	Semi-Metals	Non-Metals
Al	B	H
Ca	Si	C
Cl	As	N
Fe	Se	O
Mg	Te	F
P	I	P
K	At	S
Si		Cl
Na		Br
S		Inert gases
Ti		
Zn		

All other elements (about 60) are almost always classified as metals or trace metals. In fossil fuel ash, Si, Al, Fe, Mg, Ca, and Ti are sometimes considered as major elements, but not universally.

In this study, non-metals were not specifically considered, but when included in a table or report, they were not deleted. Some of the semi-metals are of high environmental concern (especially As and Se) and were given full trace metal status; others were included when available. The major or minor metals, or those frequently classified as such in the coal literature, become trace elements in certain systems such as cooling tower blowdown effluent or the ambient environment. Hence, all metals are usually referred to as trace metals for general use. The terminology trace element is used when the table or report includes some non-metals. The term trace metal may be used almost interchangeably in cases where the definitions are ambigguous.

Finally, the relationship between particles, particulate size and trace metals must be introduced. Concentrations of trace metals in the atmosphere are normally defined as the amount of trace metals in or on the particulate matter suspended in the air. Usually high-volume filtration is used to trap the solids and the "catch" is analyzed. Similarly, the trace metals in stack emissions frequently refer only to those associated with the particulates. The trace metals exiting the stack as vapors are seldom included. However, since the vast majority of trace metals are condensed and remain with the fly ash, trace metals are closely associated with the particulate matter in emissions or ambient air.

In certain sections of this report, a good deal of effort is devoted to particles, specifically fine particulate matter. While trace metals may not be frequently mentioned in these sections, the discussion is germane to trace metals. For example, control mechanisms are not designed for control of trace metals, but rather, are designed to control particles. Thus, trace metals are controlled only by controlling the particulate matter. This relationship is exercised frequently (in Sections 3, 4, 5, 9), and the reader should be aware of the dependence. The details of the relationship are developed in the sections mentioned above.

1.2 LITERATURE SEARCH

One of the major purposes of this project was to conduct an extensive literature search and to publish a bibliography covering trace metal emissions from SCCP's. Since much of the data gathered before 1970 is of variable quality due to the technology of the times, and computer data bases were established at about that same time, a computerized search was chosen as the principal search method. To convey the extent of the search and to inform anyone interested in extending the search (see Section 10.1), a complete review of the strategy used follows.

Three data base vendor systems were searched for information: Lockheed Retrieval Services (DIALOG®), National Library of Medicine (MEDLARS), and Department of Energy (DOE/RECON). Specific data bases searched are given in Table 1-2.

TABLE 1-2. DATABASES SEARCHED IN LITERATURE REVIEW

DOE/RECON	MEDLARS	DIALOG®
Energy Data Base	Cancer proj	Chemical condensates (Chemical Abstracts)
Energy R&D Projects	Toxline	NTIS (U.S. Government reports and announcements
	Medline	SSIE (Smithsonian Science Information Exchange)
		Excerpta Medica
		APTIC (Air Pollution Technical Information Center)
		Dissertation Abstracts
		Magazine Index
		Environmental Periodicals Bibliography
		Energyline
		BIOSIS (Biological Abstracts)
		Compendex (Engineering Index)
		Pollution
		Enviroline
		Monthly Catalogue

The search was run three times based on three requests. The first search included only coal combustion. The list of terms used appear in Table 1-3.

TABLE 1-3. TERMS USED IN INITIAL LITERATURE SEARCH

A	B	C
Coal	Trace Metals	Liquefaction
	Trace Elements	Gasification
	Heavy Metals	Fluidized Bed Combustion
	Carcinogens	
	Baghouse	SO_x, NO_x, SO_2
	Dust	Desulfurization
	Illness	Mines
	Electrostatic Precipitators	Mining
	Health	
	Fly Ash	
	Filtration	
	Scrubber	
	Toxic	

NOTE: A, B, and C are conceptual categories which may be combined or excluded.

A was "anded" with B; therefore each abstract had to have the word "coal" and one of the terms from column B. C was "notted" from A and B, which means if any term from column C was in an abstract that contained terms from A and B, the abstract was not printed.

The second search was broadened to include all combustion terms, using the word "COMBUSTION" in column A. The same terms in column B were used, but column C was expanded to include coal, mobile sources, ships, aircraft, automotive fuels, automobiles and miners.

The third request was a search on trace element or metal concentrations in ambient air, water, and soil. The strategy is listed in Table 1-4.

TABLE 1-4. TERMS USED IN THIRD LITERATURE SEARCH

A	B	C
Trace elements	Ambient	Air
Trace metals		Water
		Soil

Note: A, B, and C are conceptual categories which
may be combined or excluded

Each column was "anded" together, meaning at least one term in each column had to be included in the final abstract. Databases searched for this request included: COMPENDEX, NTIS, CHEM condensates, Monthly catalog, APTIC, Conference papers, ENVIROLINE, and Pollution.

These searches produced about 20,000 titles and abstracts. The citations were reviewed and only English language articles published in the United States and specifically referring to some aspects of trace metals and SCCP's were retained. This procedure lowered the number of relevant citations to about 2000. These abstracts were subsequentaly categorized by subject and the most useful articles obtained. About 400 documents were fully reviewed, with the balance being used only in abstract form.

It was difficult to assess the quality of foreign articles not obtained. About 20,000 English language citations were identified, with an additional 6000 foreign language articles which were not used. In the course of the study, many references were made to articles, particularly review articles, published in Britain. These have not been included.

Many of the foreign articles were in Eastern European languages or Russian. Based on the data and spot checking abstract files, it may be concluded that a considerable volume of energy-related literature exists in Eastern Europe, mostly on coal, but the quality of the research and its relevance to trace metals and SCCP's could not be determined without additional effort. A recent Southern Research Institute publication (3) reviews recent Russian literature on particulate emissions from SCCP's.

With the large volume of published works available, a manual literature search is impractical. Information retrieval from computerized information sources is the state-of-the-art. However, it was discovered that some important articles were not picked up. This was particularly true of federal government publications (such as EPA), in spite of the claims made by the data base vendors. The problem probably lies in the strategy used herein and the shortcomings of the "key wording" of the reports.

Some articles of interest were picked up from references listed in reports that were reviewed, particularly older articles. Ideally, 100 percent closure of the references was sought (that is, all key references in articles refer to already identified reports), but this was not quite achieved. It is reasonable to assume that all major articles, through at least 1977, are included within the references of this report and closure is 95 percent complete.

Some non-bibliographic references were included in the list of 2000 relevant citations, such as reports of ongoing research and research proposals. Some of these research groups were contacted to confirm the nature and the stage of the research; these data are included in the text, but not referenced in the bibliography. As a prelude to this report, EPA published in July 1978, a survey of projects relating to the CCEA program (2). Included in that report were tables of current research activities. That publication should serve as a complement to the non-bibliographic citations discussed in this report.

1.3 FORMAT AND ORGANIZATION

The report has been divided into nine sections following the introduction. Each section is designed to be read independently; that is, if a subject is encountered which is fully developed elsewhere in the report, those aspects of immediate concern are treated, but the more complete section is referenced. This leads to some duplication of references, but a complete, pertinent reference list is given at the end of each section. The references are numbered sequentially as they appear in the section.

A complete bibliography accompanies this report as a separate document. It is divided into subjects paralleling the sections. All of the referenced citations recur in the bibliography along with additional citations added for completeness. The citations under each subject category in the bibliography are alphabetized by first author's last name.

1.4 SUMMARY OF FINDINGS

Coal is our most abundant fossil fuel resource. Uncertainties in the petroleum supply and delays in the expansion of the nuclear power industry have led planners to project coal to fill the United States' ever-increasing gap between energy demand and supply. Coal reserves in the U.S. are estimated to total nearly 500 billion tons (4).

Consequently, the major emphasis of this report has been on emissions from coal-fired utilities. Not only is coal the source from which a large fraction of the SCCP-related trace metal emissions are generated, but it is also the sector that has been most studied. Oil, the other major fossil fuel energy source, annually produces less than one percent of the ash generated by coal. But because oil-fired facilities are often considered "clean" sources, particulate control may not be as efficient. The pollution contribution of oil-fired plants is probably greater than the coal-to-oil ash ratio would imply. It should not be inferred that trace metals from oil combustion are not of concern, but rather that they have not been as extensively studied as coal. The number of pages in this report concerning each type of fuel approximately reflects the proportionate amount of space in the literature devoted to that topic.

Before the SCCP trace metal contribution can be assessed, the natural or background levels of trace metals need to be determined. This is approximated by measuring ambient levels in rural locations, or locations far from any major pollution source. There is considerable doubt if any place is unaffected by anthropogenic (man-generated) trace metal pollution, but isolated locations present the only alternative. As reported in Section 2, an ambient air monitoring network has been established under the auspices of the EPA. Data are regularly fed into the SAROAD (Storage and Retrieval of Aerometric Data) database, but most of these data are on criteria pollutants. Criteria pollutants are SO_2, NO_x, CO, hydrocarbons and particulate matter. In general, the particulate matter data gives little information about trace metal concentrations. However, for some 400 stations trace metal data averaged over three months are also fed into the SAROAD database.

Two recently published reports (5, 6) have summarized non-criteria pollutant data through 1975. Additional information may be available from state offices or regional EPA offices, but each case is individual. With lead's becoming a criteria pollutant (7), the data on trace metals are expected to increase.

Outside of this SAROAD network, data are fragmented geographically and of uneven quality. Most measurements were taken to serve some specific purpose, frequently in an urban area or around a major pollution source. Seldom is the information of high enough quality to specifically identify any pollutant source, such as an SCCP. The data on water and soil trace metal levels are too locale specific to attempt any generalization.

Turning to SCCP pollution sources, the first consideration is the fuel itself. Section 3 quantitatively reviews the trace metal levels in coal (the main anthropogenic pollution source), oil, gas, refuse and wood. In general, the trace element levels in coal are about the same as they are in the earth's crust. The burning of coal concentrates them about tenfold, but releases some to the atmosphere with the rest remaining in the ash (solid waste) from the combustion processes. Oil has less than 0.1 percent ash with the most abundant trace metals being vanadium and nickel. Natural gas has essentially no trace metals. Municipal refuse has about the same ash content as coal (~10 percent) and has concentrations of many trace metals comparable to levels in coal. Little has been studied for trace elements associated with combustion of wood.

Section 4 discusses the details of various types of SCCP's. It is necessary to understand how different combustion processes function in order to understand the nature of the problem they create. All the potential wastestreams and their usual contents are reviewed. Although solid and liquid wastes do contain trace metals, the wastestream of greatest concern is the flue gas and fly ash, particularly from coal and refuse. Therefore, the major emphasis of the section is on control technologies. They have the largest impact on the atmospheric emissions and also offer the greatest range of alternatives. Several control technologies have been developed to control criteria pollutants: SO_2, NO_x and particulates. Control of the particulates also represents control of the trace metals. However, many of the trace metals are known to be highly concentrated in the very fine fly ash particles, the "fines." These particles are commonly defined as the fraction smaller than one micron. They present problems for several reasons: (1) they are most mobile and have the longest residence times in the atmosphere; (2) they contain higher concentrations of trace metals; and (3) they are easily inhaled and difficult for the lungs to eliminate.

Section 5 quantitatively reviews the literature on point-source emissions. Again the main emphasis is on coal. Data are presented from several studies which follow trace metals through a combustion process from source through burning through scrubbing to emission. What is known about how and why the trace metals partition as they do is documented. The emissions in all effluent streams from coal, oil, gas refuse, and wood combustion in a variety of processes are presented and discussed. The efficiencies of different control technologies discussed qualitatively in Section 4 are quantified in Section 5.

Section 6 is devoted to the health and environmental effects of trace metals. Specific notice has been made where effects can be directly related to SCCP's trace metal emissions. More generally, however, the literature reports health and environmental effects due to trace metals independent of source. A large table gives the specific health and environmental effects caused by each trace element. Environmental pathways and transport mechanisms are also discussed.

Section 7 deals with the radiological trace metals from SCCP's. This section reviews source, emission and health data related specifically to the radionuclides. The consensus of research is that, while coal burning plants emit higher levels of radiation than nuclear power plants, the levels are still so small as to be of minor concern compared with the criteria pollutants and other trace metals.

Section 8 addresses the accuracy of data. The quality of data was extremely variable before 1976, when an NBS standard coal and coal ash greatly aided researchers in establishing the validity of their data. Part of the reason for the uneven quality of data was the variety of analytical techniques used. Each method has its strong and weak points, and one must use extreme caution when comparing data from different laboratories. Very recently, the advent of large computers has enabled researchers to use neutron activation analysis and X-ray fluorescence with a high degree of accuracy. Neither of these methods requires sample preparation, and the results are remarkably consistent among different laboratories. New simultaneous, multi-element analysis techniques should also serve to greatly increase the quality and quantity of trace metal data.

Section 9 reviews the current status of regulations that pertain to trace metals. The net finding is that there are essentially no regulations for trace metals, per se. The closest any regulations come to controlling trace metal emissions are the regulations for particulate emissions. Very recently, states are beginning to promulgate regulations so detailed as to set specific emissions limits for different sized fly ash particles. In some instances, control of fine particles is synonymous with trace metal control. This is in part directed at better trace metal control. The recent designation of lead as a criteria pollutant indicates the increased interest in regulation of trace metal emissions.

Section 10 reports on needs for future research recommended in the literature. Also some research needs are apparent from obvious gaps in the literature. At the end of each of the other sections (except Section 1) is a subsection which deals specifically with the research needs identified in that subject area. These research needs are of two general types: (1) to fill in data gaps (for example in ambient air monitoring), and (2) to expand or explore our knowledge of trace metal processes (for example in the particle size or health field). A summary of the discussion of research needs found near the end of each of the eight subject areas sections, combined with Section 10, should represent a survey of the more important future research topics.

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SECTION 2

AMBIENT TRACE METAL CONDITIONS

Perhaps the first point to be addressed in the assessment of the impact of trace metal emissions from SCCP's is the present ambient levels. The atmosphere is the medium of greatest concern, and the individual can do little to protect himself from its pollutants. These pollutants may be widespread and long lasting; they also may have a significant impact on human health.

The water and soil are also of concern, but in these media the impact of a pollutant source may be much more localized and more readily identified. Any data on trace metals in the water or soil are so dependent upon local factors such as population, industry, and geographical and meteorological conditions that comparisons are very difficult. These media are of great concern, but because the problems, the studies, and the solutions are usually local issues, no general statements can be made.

The atmosphere provides a large ballast for pollutions. Trace metal pollutants may have long residence times, undergo mixing and move far from their source. Although the atmosphere is also very dependent upon local factors, boundaries are more gradual, and monitoring over regions provides useful information on pollution sources, build-up and the effectiveness of control strategies. Such data may also prove useful in public health studies.

2.1 AMBIENT TRACE METAL CONCENTRATIONS

For some time, the United States has had an air pollution monitoring network. However, its chief concern has been the criteria pollutants: NO_x, SO_2, CO, hydrocarbons and particulates. Until very recently, no direct attention was paid to trace metals.

Atmospheric trace metals concentrations are measured by pulling a high volume of air through a filter ("HiVol" sampling) to trap out the suspended particulates. These filter catches are then analyzed for the amount of trace metals, and by knowing the volume of air sampled, the trace metal concentration in the atmosphere is calculated.

EPA receives information from an air monitoring network with about 10,000 stations (1). However, this network was established to gather data on criteria pollutants, and only a few trace metal data have been included. About 400 stations report trace element data on about 27 elements, 21 of which may be considered as trace metals (2). While these data are not dense enough to allow construction of regional isopleths, they do provide a good overview of the ambient concentrations of trace metals in the U.S. atmosphere. And, although the data are averaged and condensed before being fed into the national database, and although the results are relatively uniform because all analyses are done by EPA-RTP, the results are not analyzed or interpreted on a regular basis. The resulting publications merely display the data.

In 1957, the National Air Sampling Network (NASN), later called the National Air Surveillance Network, consisted of 185 urban and 48 rural stations. By 1971, there were 1141 urban, 66 source-oriented (i.e., associated with a specific point source) and 49 rural stations in the network. As mentioned above, the prinicipal function of the network is to monitor criteria pollutants, but some trace metal data have resulted. In 1972, the EPA published the data from NASN for the years 1964 through 1968, including the non-criteria data (3). They reported as many as 16 trace metals, but 5 elements are incomplete (antimony, bismuth, copper molybdenum, and tin). The ranges and most common values for the other 11 are given in Table 2-1.

Since 1968 most of the nation's air pollution monitoring has been carried out by three NASN's: high volume-network, gas sampling network and the CAMP (Continuous Air Monitoring Program) station network. This total program, operated under the auspices of the EPA, consisted of some 7,000 air samplers (1).

TABLE 2-1. ATMOSPHERIC METAL CONCENTRATIONS IN U.S., 1966-1967

	Urban ($\mu g/m^3$)				Non-urban ($\mu g/m^3$)			
Element	Value Detected	Range	Detection Limit	% Below Detection Limit	Most Common Value Detected	Range	Detection Limit	% Below Detection Limit
Be	.0003	0-.0007	.0002	85	.00007	0-.0004	.0007	95
Cd	.01	0-.09	.01	73	.004	0-.03	.004	93
Cr	.006	0-0.1	.006	62	.003	0-.03	.002	70
Co	.006	0-.045	.006	99	--	--	.002	99.5
Fe	1.5	0.1-6.1	.2	3	.2	.02-1.5	.05	17
Pb	.8	0.1-5.0	.1	1	.08	.03-0.8	.03	28
Mn	.03	0-.81	.01	6	.01	.002-.07	.004	21
Ni	.01	0-.187	.006	30	.002	0-.03	.002	36
Ti	.02	0-.13	.001	51	.002	0-.03	.003	28
V	.02	0-.905	.003	40	.003	0-.01	.001	55
Zn	.5	0-1.7	.1	60	.1	0-0.6	.04	56

SOURCE: (1)

Monitoring and data analysis are carried out within the Office of Air and Water Programs at RTP, which, with its Air Pollution Technical Information Center, is a subdivision of the EPA. Processing of the huge amounts of data is handled by an automatic system for the Storage and Retrieval of Aerometric Data (SAROAD). The SAROAD system is part of the Atmospheric and Emissions Reporting System (AEROS). The collection and dissemination of aerometric data to and from the National Aerometric Data Bank (NADB) are handled through the National Aerometric Data Information Service (NADIS). Again, it should be emphasized that these data are mainly for criteria pollutants, and trace metal data are reported for only about 400 stations. Quarterly reports are issued for criteria pollutants, but only infrequent summary reports for non-criteria pollutants have been forthcoming. Information on trace element concentrations in the atmosphere is not required by any Federal agency (4).

The Monitoring and Data Analysis Division of EPA has recently published two reports that present air quality data for non-criteria pollutants; the first covers the years 1965-1974 (5) and the second covers the years 1971-1975 (2). Both of these are vast data compilations, without comment. They cover about 400 reporting stations from all 50 states and include rural and urban stations. These data are averaged over three month periods and processed at the state or EPA regional offices before being submitted into the SAROAD system. Thus, more complete or detailed data may exist at the local offices, but each case would require individual attention. The data are so voluminous that no representative one-page table is possible. Again, it should be noted that the bulk of data in the SAROAD system are for criteria pollutants, and customized retrieval is required to access the latest trace metal data.

Studies outside of AEROS more often present some data analysis and commentary, but are very spotty and uneven. The methods of sampling and analysis are not uniform, and the studies were usually generated for some specific reason.

One such study was an EPA supported project that measured the trace elements in ambient air at five selected stations in the Northern Great

Plains (6). Table 2-2 summarizes these data; however, 5 data points over about 100,000 square miles is only dense enough to give an overview of this essentially rural area. The study was commissioned because of suspected ambient trace metal increases due to industry, coal burning and coal processing in the area. One of the results was the confirmation that glass substrate filters mask low level trace metal concentrations (due to trace metals in the substrate); cellulose filters are now preferred.

Representative of urban studies is one reported for Sacramento, California (7). These data, taken on sized aerosols, are presented for particulates below 3.6 μm, those sizes most respirable; see Table 2-3.

Urban air concentrations are being studied by the International Decade of Ocean Exploration. Their values for the concentration of trace elements in U.S. urban air are presented in Table 2-4. The values in Table 2-4 represent an averaged value of U.S. urban air concentrations from over 20 urban locations around the U.S. (8). Other research teams have reported background trace element concentrations in urban aerosols for Miami, Florida (10), Fresno, California (11), New York City (12), northwest Indiana (13), and several Texas gulf coast cities (14). Typical of some states, Texas has established an air particulate monitoring system with trace element analysis. While this program is focusing on the major urban areas, a few smaller cities were included. Table 2-5 gives an analysis for up to 17 elements at various sites around the state (14). Also see Table 2-6 for a similar California study (7).

One isolated study did try to establish background levels for atmospheric trace metals (15). It was remote from any large fossil fuel power plant, and the researchers hoped to determine "natural" ambient (background) levels before coal-fired plants began operation in adjacent states. The site chosen was rural Chadron, Nebraska, 480 km north-northeast of Denver, Colorado. Rather than collect particulates by high-volume sampling, they collected and analyzed rain and snow for seven metals. Their results are reproduced in Table 2-7.

TABLE 2-2. AMBIENT TRACE ELEMENT CONCENTRATIONS BASED ON FIVE NORTHERN GREAT PLAINS' SITES

Element	Annual Range μg/m^3	Annual Average μg/m^3
Arsenic	4E-3/4E-5	4.32 E-4
Barium	3E-2/9E-4	9.10 E-3
Beryllium	5E-5/4E-6	1.68 E-5
Calcium	3E-0/2E-5	5.55 E-1
Cadmium	2E-4/2E-5	6.95 E-5
Chlorine	3E-1/1E-5	5.66 E-2
Cobalt	6E-4/8E-6	1.34 E-4
Copper	3E-2/3E-3	1.54 E-2
Chromium	4E-2/2E-3	1.03 E-2
Fluorine	4E-1/4E-3	6.26 E-2
Iron	4E-1/6E-3	1.14 E-1
Lead	5E-2/2E-3	1.66 E-2
Lithium	2E-3/2E-5	1.66 E-2
Magnesium	6E-1/8E-3	1.99 E-1
Manganese	2E-2/7E-4	3.88 E-3
Nickel	5E-3/2E-5	1.32 E-3
Phosphorus	3E-1/2E-2	8.70 E-2
Selenium	5E-4/2E-5	1.59 E-4
Silicon	3E-0/9E+1	3.56 E+1
Silver	2E-4/2E-6	3.41 E-5
Sodium	2E-0/3E-2	5.44 E-1
Zinc	3E-2/4E-3	1.21 E-2

SOURCE: (6)

TABLE 2-3. COMPARISON OF AMBIENT TRACE ELEMENT DATA FOR SACRAMENTO, CALIFORNIA (JANUARY, 1974) BASED ON MULTIDAY IMPACTOR SAMPLES WITH IMPACT MODEL RESULTS

Element	Stage 2 Filter Concentration (μg/m³) 0.65-3.6 μm Size Range	Stage 3 Filter Concentration (μg/m³) 0.1-0.65 μm Size Range	Combined Concentration (μg/m³) 0.1-3.6 μm Size Range
Ba	1.0×10^{-3}	0.0	1.0×10^{-3}
Ca	6.5×10^{-2}	3.9×10^{-2}	1.0×10^{-1}
Cl	1.87×10^{-1}	0.0	1.9×10^{-1}
Cr	0.0	1.0×10^{-2}	1.0×10^{-2}
Cu	3.0×10^{-3}	1.4×10^{-2}	1.7×10^{-2}
Fe	8.6×10^{-2}	1.0×10^{-1}	1.9×10^{-1}
Mg	2.0×10^{-2}	3.0×10^{-3}	2.3×10^{-2}
Mn	3.0×10^{-3}	1.0×10^{-3}	4.0×10^{-3}
Na	1.06×10^{-1}	5.7×10^{-2}	1.6×10^{-1}
Ni	0.0	2.0×10^{-3}	2.0×10^{-3}
Pb	1.64×10^{-1}	7.22×10^{-1}	8.9×10^{-1}
Si	1.66×10^{-1}	1.56×10^{-1}	3.2×10^{-1}
Zn	1.6×10^{-2}	2.6×10^{-2}	4.2×10^{-2}

SOURCE: (7)

TABLE 2-4. AMBIENT TRACE METAL CONCENTRATIONS OFTEN USED FOR REFERENCE

Element	Crustal[a] Abundance (ppm)	Open[b] Ocean (ppm)	U.S. Urban[b] Air Average (μg/m^{3})
Aluminum	81,300	1,000	1,500
Antimony	0.2	200	20
Arsenic	1.8	2,000	20
Beryllium	2.8	5	1
Cadmium	0.2	20	20
Cesium	60	300	4
Chromium	100	300	40
Cobalt	25	30	2
Copper	55	2,000	200
Gallium	15	20	1
Iron	50,000	5,000	2,000
Lanthanum	30	10	3
Lead	13	20	1,000
Manganese	950	300	200
Mercury	0.08	100	3
Molbydenum	1.5	10,000	10
Nickel	75	2,000	30
Scandium	22	1	1
Selenium	0.05	100	4
Silver	0.07	10	2
Tantalum	2	20	0.2
Tin	2	20	20
Titanium	4,400	1,000	100
Tungsten	1.5	100	5
Uranium	1.8	3,000	0.1
Vanadium	135	1,000	200
Zinc	70	3,000	700

[a] SOURCE: (9)

[b] SOURCE: (8)

TABLE 2-5. CONCENTRATION OF ELEMENTS IN AIR PARTICULATE MATTER IN TEXAS

Location	Element (μg/m^3)										
	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg
Statewide (range)	7.73 (0.6-29.9)*	0.19 (.02-1.33)	- (<.004)	0.03 (<.05-1.1)	0.05 (.02-.17)	1.3 (0.1-10)	<.018 (<.018-.05)	- (<.01)	0.12 (<.01-.96)	0.13 (<.005-1.77)	- (<.02-.05)
Amarillo	2.7	0.34	<.006	0.01	0.05	1.5	<0.02	<0.01	0.12	0.15	<0.03
Clute	29.9	0.22	<.007	0.01	0.01	1.0	<0.02	<0.01	0.01	0.11	<0.03
Corpus Christi	21.9	0.29	<.008	1.10	0.09	10.0	<0.02	<0.01	0.16	1.77	<0.03
Dallas	4.8	0.08	<0.004	0.01	0.01	0.7	<0.01	<0.01	0.02	0.01	<0.02
El Paso	13.7	0.34	<.008	<0.06	0.11	3.4	<0.02	<0.01	0.96	1.66	<0.03
Houston	6.6	0.11	<0.008	0.05	<0.03	0.6	<0.03	<0.01	0.22	0.14	<0.03
Harlingen	11.8	0.20	<0.006	<0.05	<0.03	1.2	<0.02	<0.01	0.02	0.02	<0.03
San Antonio	3.5	0.12	<0.004	<0.04	<0.02	0.1	<0.01	<0.01	<0.01	0.07	<0.02

* Valves in parenthesis are ranges

SOURCE: (14)

TABLE 2-6. AVERAGE AMOUNT OF TRACE ELEMENTS IN SELECTED CALIFORNIA CITIES.

	ELEMENTS * (ppb)														
Site +	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Mn	Fe	Cu	Zn	Br	Pb
Sacramento	617	133	869	3372	1016	336	591	527	94	6	36	1215	8	30	158	704
Richmond	1692	122	134	1058	1181	1948	296	412	40	22	7	634	4	75	125	557
Livermore	302	92	357	2382	609	244	331	454	64	6	30	934	5	60	65	361
Oakland	1710	137	115	1339	1258	2014	313	528	72	26	36	764	26	132	221	984
San Jose	732	197	597	3145	869	891	470	836	91	5	30	1182	5	58	288	1058
Salinas	715	89	196	1134	532	1048	219	285	24	7	12	440	2	5	35	179
Bakersfield	169	77	1420	4566	1507	18	1043	1252	146	19	27	1819	14	47	252	1072
Los Alamitos	825	173	472	2149	3879	366	451	642	79	71	27	973	6	73	115	940
Los Angeles	696	98	443	2418	4013	123	473	751	134	25	31	1006	17	183	252	1498
Azusa	478	167	1137	3751	3084	97	913	1063	242	43	49	2009	20	190	217	1407
Riverside	274	94	1024	4019	2884	107	793	1266	143	15	36	1793	7	95	370	1697
Indio	320	182	2434	7864	3409	99	1554	2619	312	35	70	3387	14	108	119	789
El Cajon	890	193	875	3680	2663	296	560	772	139	24	33	1327	7	39	166	1041

*Nominal error, ±15%   + for months July, August, September (1973)

Source: (7)

TABLE 2-7. CHADRON, NEBRASKA RAINFALL ANALYSIS, 1973

Element	Concentration g/cm^3
Ag	8.4×10^{-11}
Al	3.5×10^{-7}
Cd	3.1×10^{-10}
Cu	4.4×10^{-9}
Mn	5.2×10^{-9}
Pb	4.8×10^{-9}
Zn	1.0×10^{-8}

SOURCE: (15)

The study of trace metal concentrations in aqueous systems is currently hindered by the lack of a convenient or obvious reference or standard. Therefore, some authors (8) have chosen the trace element concentrations of the open ocean as an universal reference point, much like the crustal abundances are used for terrestrial comparisons. Trace element concentrations in oceans and crustal abundances are given in Table 2-4. Another set of values used for comparison are the Multimedia Environmental Goals (MEG's). These are concentrations of pollutants, including trace metals, thought to be safe for human health or non-deleterious to the environment. Values are given for both emission goals, Minimum Acute Toxicity Effluents (MATE's), and Ambient Goals, Estimated Permissible Concentrations (EPC's); see Section 9 (Table 9-6). In addition, another value often used as a guideline in estimating permissible effluent stream concentrations is the U.S. Department of Agriculture irrigation standards for water considered safe for agricultural irrigation (17). The trace metal concentrations of our surface waters (which show great fluctuations both in location and time) and groundwaters remain largely unknown.

In general, the aqueous trace metal concentrations are so dependent upon local population, industry and geological factors, as well as the amount of water moving through a region, that it is futile to even present typical or representative values because none can be defined.

No general statements can be made about trace metal concentrations in soils. The average crustal abundances are well known (the Clarke values) and often used as a standard for comparison (see Table 2-4); however, local factors are so variable and significant that ambient soil concentrations must be measured for each individual case. Several such studies are discussed in Sections 6.2.2 and 6.2.3 (18-24). As with aqueous systems, typical or representative values cannot be presented.

2.2 NATURAL SOURCES OF TRACE METAL POLLUTANTS

A natural source may be defined as any source not man-made or man caused (not anthropogenic). Wind, rain, flowing water and other meteorological factors are examples of natural emission pathways. In some rural areas, such as West Texas, the majority of airborne trace elements are due to windblown particles (25, 26). Another indirect but significant pathway of trace metals into the biosphere is uptake by plants. The trace metal may be mobilized by the action of the plant (e.g., respiration, spores), or the vegetation may be consumed by animals including, directly or indirectly, man. Pathways through living systems are dealt with extensively in Section 6.2 of this report.

Background concentrations of trace elements in streams, rivers, and lakes have not been well quantified (27). One reason for the lack of more complete information is simply the magnitude of the task; however, several studies do exist on watersheds near large electrical utility boilers (28-30) in which quantification of trace elements in air, soil, and water are considered. In most of these studies, attempts were made to determine the background levels and the amounts of trace metals mobilized via natural pathways and man; also see Section 6.2 and 6.3.

2.3 ANTHROPOGENIC SOURCES OF TRACE METAL POLLUTANTS

The escalating concern about the environment over the last several decades has been due, in part, to the increasing generation of electric power (31-34). More recently, the use of coal, which produces two to three orders of magnitude more ash than oil or gas for the same Btu output, has increased; see Sections 3 and 5 of this report for quantification. The continuing growth of urban areas and industry have also contributed to the environmental problems.

The trace metals emitted by the burning of fossil fuels and urban refuse are predominantly associated with the ash. Trace metals such as mercury, molybdenum, beryllium and lead and trace (non-metallic) elements such as selenium, arsenic, fluorine and chlorine may be emitted at least partially in the vapor phase, and present unique problems. However, in most cases, extensive evidence exists showing that the trace metals are intimately bound to the bottom ash and aerosol fly ash. In fact, many of the trace metals are concentrated in the submicron ash particles (35); see Sections 3.4, 4.8.3 and 5.5.

Determination of the relationship between trace metals and ash particles is still evolving, and in general, not enough is known about the location, quantity, mobility and environmental and health effects of trace metals to fully characterize the relationship. Thus, in the past, most attention was focused on particulate emissions which could easily be quantified. Within the last decade, the trace metals themselves have begun to be studied. Still, most of the control technology and regulations are designed to moderate or curtail particulate emissions. Of course, a decrease in particulate emissions means a concomitant decrease in trace metal emissions, but not necessarily proportionately so. In fact, the current trend in regulations is to establish limits on fine particulate emissions in an attempt to reduce trace metal emissions. For example, New Mexico now has regulations limiting the release of sub-2.0 μm particles from coal-fired power plants (36). Today, only two trace metals are classified as hazardous emissions; mercury and beryllium (37), and very recently (October 1978) lead has been declared as a criteria pollutant (38); see Section 9. Thus, essentially all our knowledge about atmospheric trace metal levels comes from studies of particulate matter.

Although coal burning does not produce a liquid effluent directly, aqueous effluent streams do result from coal combustion processes. The main sources are either from the sluicing of ash or from the wet SO_2 scrubbers. In both cases, ash contacts water and the trace elements may be leached into the aqueous phase. See Section 4 for a full description of all process streams. These liquid effluents are normally cleaned to some extent and either reused, released or ponded where the water may soak into the soil. Also, buried ash may be leached by natural waters and release trace metals. Any of these processes may generate aqueous trace metal effluents (39). These sources are usually rather visible (except underground leaching) and easily traced to the source. As a result, they have been fairly well identified. Some states now do not permit aqueous discharge from new power plants.

Concentrations of trace elements in soils have been determined only in widely scattered regions of the U.S. In studies of SCCP's, trace element concentrations of soils have been measured around large SCCP's to determine long term soil effects of emitted trace elements (18, 27,30, 40, 41). For example, in one study done in conjunction with a trace element balance around Mohave Generating Station in Southern Nevada, the concentration of specific trace elements in soil was determined (41). The sampling was done on specified soil types up to 20 kilometers downwind of the smokestack. Soil profiles up to 20 centimeters deep were determined and all trace metals studied, except strontium, were found to be greater in the surface soils (0-2 cm). Sulfur, copper and strontium were found to decrease in surface soils with increasing distance from the plant. Estimations of the deposition during the lifetime of the plant showed that the emission rates were inadequate, except for sulfur, to account for the measureable increases that were found in soil concentrations. Two other studies were recently performed in conjunction with the establishment of trace element balances around watersheds near large SCCP's (18, 30). In one study performed in Tennessee, a six-month mass balance indicated that the watershed under study efficiently retained lead, cadmium, and copper; however, less than 70 percent of magnesium, chromium, zinc, and mercury introduced to the watershed could be retained by the soil (18).

Combustion of fossil fuels and wood in smaller SCCP's (e.g., industrial boilers, commercial package boilers, residential heating) contributes to the anthropogenic emissions, but very little data were found for these processes. The paucity of data on residential units was particularly obvious. Some emission studies have been done on package or self-contained boilers, but rarely were trace metals included within the scope of these studies. Once again, studies principally concerned with particulate loading represent the main source of trace metal data. See Section 5 for a report of these studies.

The Air Pollution Control Act was promulgated in 1955 by the Congress. The major provisions of the act stipulated that the Federal government would provide research funds and technical assistance for studying the causes of pollution. The states and local governments would be responsible for pollution control at the source (1). By 1976 over 200,000 anthropogenic sources of pollution had been identified as being subject to emissions limitations (42). Of the 200,000 sources of emissions, about 20,000 are classified as major emitters (emissions greater than 100 tons/yr) and are projected to produce 85 percent of all stationary source air pollution. Table 2-8 shows the degree of compliance attained by the major emitters and priority sources (see table for definition) as of 1975 (42).

Thus, although this act applies only to criteria pollutants (SO_2, NO_x, CO, hydrocarbons, and particulate matter), it is representative of the laws and regulations that limit emissions. Until the level of knowledge about trace metals is improved, regulations and control strategies will continue to apply only to criteria pollutants. Lead is the first example of a specific trace metal that is being regulated (38).

There are other anthropogenic sources of trace metals, but most of these do not fall under the definition of SCCP sources (e.g., mobile sources, process heating, coal gasification, refineries). Although urban refuse is comparable to coal in ash content per Btu, far less is burned, and coal remains as the primary source of trace metal emission from SCCP's.

2.3.1 Urban Environments

Current background trace element concentrations are, at best, difficult to ascertain for most urban areas. For example, Ca, Ti, V, Mn, Fe, Ni, Zn, Br, and Pb, have all shown order of magnitude fluctuations in a two-hour sampling time (11). Most atmospheric trace metal studies use high-volume filtration sampling methods. They result in the collection of suspended particles or aerosols. These filtrate "catches" are then analyzed and represent the atmospheric trace element concentrations; however, the collection and analysis of aerosols is deceptively complex, and the quality of the data is often suspect.

TABLE 2-8. COMPLIANCE STATUS OF NATIONAL PRIORITY SOURCES[a]

(Type of Source/ Primary Pollutant)	Total Number Identified	Status with Respect to Emission Limitation and/or Compliance Schedule		
		In Compliance	In Violation	Unknown Status
I. All Major Sources (e.g. sources capable of emitting 100+ tons/yr of a pollutant)	19,360	16,190 (84%)	2,136 (11%)	1,035 (5%)
II. Priority Major Sources				
A. Power Plants (SO_x)	383	276 (72%)	60 (16%)	47 (12%)
B. Smelters (SO_x)	25	5 (20%)	4 (16%)	16 (14%)
C. Steel Processes (Particulates)	1,177	449 (38%)	301 (26%)	427 (36%)
D. Municipal Incinerators	230	110 (48%)	85 (37%)	35 (15%)
E. Petroleum Refineries (HC)	260	173 (67%)	34 (13%)	53 (20%)
F. Kraft and Sulfite Pulp Mills (SO_4)	150	87 (58%)	34 (23%)	29 (19%)

[a] Numbers represent facilities rather than emission points for all source categories.

SOURCE: (42)

For example, it has been reported that the size distribution of urban aerosols often has two modes separated by a particle-deficient region at approximately 1-2 microns. This deficiency may be in part caused by emission from SCCP's. The removal efficiency of modern electrostatic precipitators frequently used with large coal-fired boilers decreases rapidly for particles smaller than one micron. Thus, they emit primarily small particles and may be a significant contributor to the modal distribution below one micron found in many urban aerosols (35); also see Section 4 of this report. Particle sizes below three microns are known to be easily respired by humans, and such particles tend to reside for long periods in the lungs; see Section 6.4 of this report for a detailed discussion.

Another theory that has been advanced is that the bimodality of urban aerosols may be the result of different formation processes for the two-size modes (43). Hence, any attempt to identify aerosol sources by means of elemental composition "fingerprinting" should therefore include measurements of aerosol composition as a function of particle size (44, 45). Many reported studies of urban aerosols have not done this.

Since much of the particulate matter in the atmosphere is derived ultimately from crustal material (e.g., particles from wind erosion of soil and rocks, fly ash particles released in coal combustion), a common method of reporting urban trace element concentrations is the use of enrichment factors. As reported by Gordon and Zoller (46), an enrichment factor of a particular element is determined by first comparing its urban concentration to its crustal abundance. This ratio is then compared to a non-volatile element whose concentration is known to be quite stable. Gordon and Zoller chose aluminum. Numbers greater than one are then concentrated relative to aluminum. Figure 2-1 shows such enrichment factors obtained from concentrations of elements measured on atmospheric particles collected in Boston, northwest Indiana, and San Francisco (13, 46, 47).

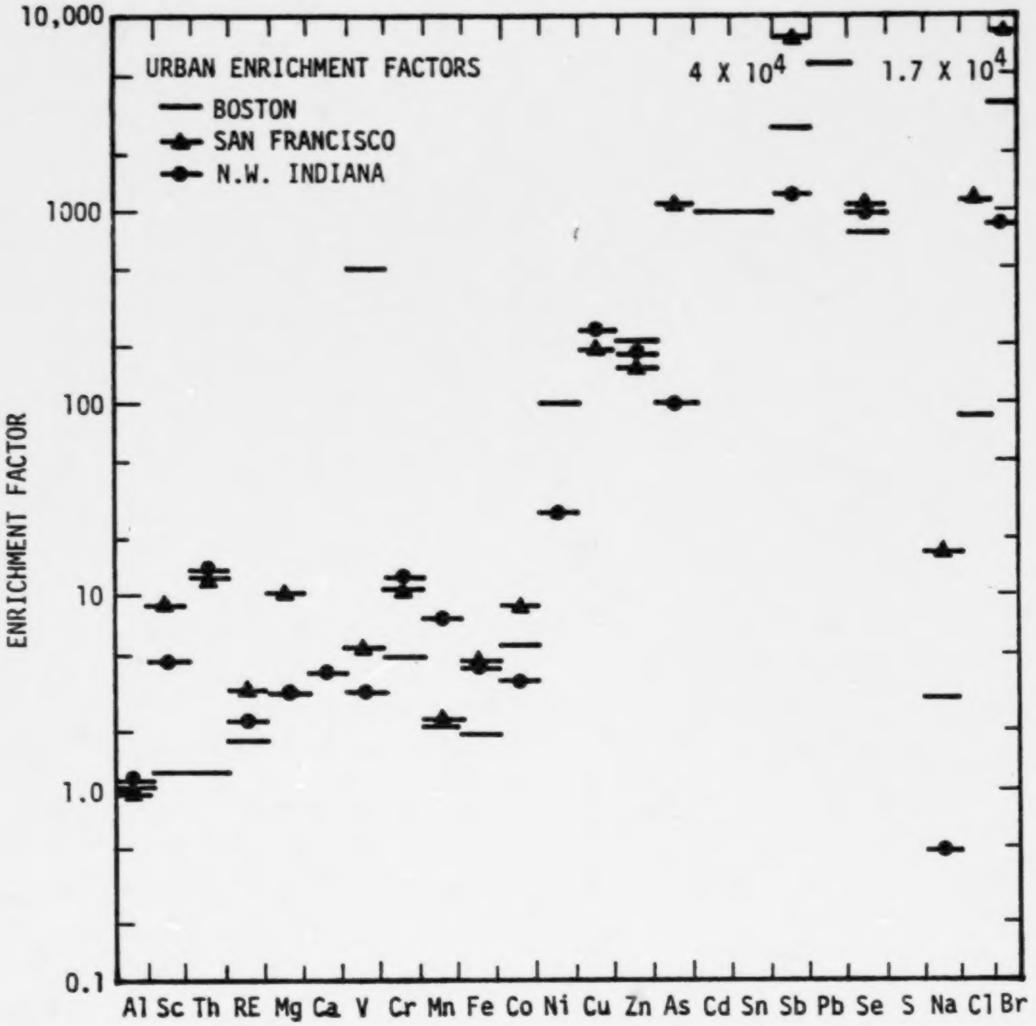

Figure 2-1. Enrichment factors relative to aluminum for elements on particles collected in the atmospheres of Boston, northwest Indiana, and San Francisco. In this figure "RE" represents an average of four rate-earth elements.

SOURCE: (46)

Some programs which measure ambient levels of trace metals are designed to identify large fluctuations. Few of these programs are designed to identify the source(s). One project by Giauque, et al. (11) which did use this approach studied Fresno, California. They sized the urban aerosols before measuring the trace metal concentrations. Some of their conclusions were:

- Seventy-five percent of lead and bromine and 50 percent of zinc were found on particles less than 0.5 μm in diameter. The lead and bromine were predominantly from automobiles; zinc was probably derived from incineration of tin cans and tires.
- Diurnal concentration fluctuations were noted for Pb, Br, Ca, Zn, Cr, Fe, K, Ti, Mn. The last four of these showed fluctuations similar to total particulate loading cycles and are probably derived from windblown dust.
- Calcium was found predominantly on large particles. Its source is most likely the cement industry.

Also, the Sacramento study reported earlier, see Table 2-3, performed limited particle sizing before trace element analysis (7).

The current interest in this area is to attempt to use emissions data and modeling to "predict" the reported ambient trace metal levels. Research in this direction requires a system capable of inputing emission rates for all local point sources (available from source emission inventories such as the National Environmental Data System, NEDS) and modeling their distribution to predict trace metal ambient concentration patterns. Comparison with measured ambient isopleths could then be used to improve the modeling until a full understanding of the pollution pattern was achieved. In general, the state-of-the-art has not reached this level. Local studies of many cities have been made, but few were published and/or identified by this information-literature search. Among those areas studied where the researchers speculate to some degree about the sources of trace metal pollutants are studies of Miami, Florida (10), New York City (12), northwest Indiana (13), Boston (46), and several Texas (14) and California cities (7). Data from the Texas and California studies were given in Tables 2-5 and 2-6.

2.3.2 Rural Situations

The influence of SCCP's on trace element concentrations of the rural United States is also difficult to assess. One reason is that the impetus for determining most of the rural data has been the study of large fossil fuel power plants located in a particular rural area (15, 48-52). Seldom was any preliminary or background study done. Thus, a study commenced after the plant has been in operation cannot accurately determine the contribution due to the SCCP. Also, much of the particulate matter in rural areas is due to windblown dust, and the contribution of the fly ash is sometimes relatively small. Finally, the far smaller number of people affected in rural areas by SCCP emissions is a contributing factor, both financially and politically, to the lack of motivation to study rural regions.

The Chadron, Nebraska study was mentioned above in Section 2.1. Another study in rural Colorado (50) reported background beryllium levels of 0.4 $\mu g/m^3$ in air. The study projected that if coal combustion were increased four-fold, airborne beryllium levels would rise to 1-2 $\mu g/m^3$. This beryllium concentration level is a normal background level experienced in industrial areas of the United States. Another study looked at emissions of cadmium and attempted to identify the sources (53). The results of the study appear in Table 2-9.

TABLE 2-9. CADMIUM EMISSION RATES

Source	Emission (1000 lbs/yr)
Metal Extraction	0.5
Concentration and Metal Production	2,100.
Conversion of Metal to Products	33
Product Use	36
Metal Recycle and Disposal	2,200
Fossil Fuel Combustion	200-700
Phosphate Fertilizer Production	50.

SOURCE: (53)

The Texas study also included several small, non-urban towns (14), see Table 2-5, as did the California study, see Table 2-6.

2.3.3 Nonspecific Sources

The specific contribution of SCCP's to background trace element concentrations is an area that is currently experiencing increased interest and investigation. However, under the current regulatory climate, there is no law that specifically requires the reporting of trace element emissions from SCCP's. Therefore, we are only able to report on how well plants with fossil-fueled boilers have responded to other requirements under current regulations. Of special interest should be their compliance with requirements for total suspended particulate standards. Of 20,000 major emitters of particles identified in 1974, less than 400 were coal-fired power plants (42). Data for compliance of SCCP's with regards to total suspended particulate standards was not available as a separate category in 1975. By comparison, with regard to regulatory SO_2 laws in 1974, some 72 percent of coal-fired power plants were in compliance (42).

Many studies have been done that considered particular trace elements such as boron, beryllium, bromine, copper, manganese, lead, selenium and zinc emissions into the biosphere. Some of these studies also estimated the amounts of a particular element emitted by coal combustion (50, 63-65). In a similar vein, the 1969 copper emissions to the atmosphere in the U.S. amounted to 13,680 tons. The combustion of coal was responsible for only 15% of the total copper emissions (56,57). In 1972, boron emissions to the atmosphere in the USA totaled 11,003 tons. Nearly 22% of the emissions resulted from the processing of boron compounds, more than 34% from the manufacture and use of various end products, and about 43% from the combustion of coal (55). For manganese, normal background levels range from 0.01 - 0.02 $\mu g/m^3$. At power stations using methylcyclopentadienyl manganese tricarbonyl as a smoke suppressant for stack emissions, air concentrations of manganese 1000 feet downwind were 0.1 - 0.2 $\mu g/m^3$. At a site burning fuel oil containing 125 ppm manganese, air concentrations 1,500 feet downwind were 0.03 - 0.05 $\mu g/m^3$ (53).

In another study selenium emission rates from the Allen Steam Plant study were used to calculate the minimum mobilization of selenium from coal consumption in the United States and the world. Calculations indicate that 1.5 to 2.5 times as much selenium is mobilized by man through coal burning as by natural weathering (58).

The mass balance of trace elements in Walker Branch Watershed in relation to nearby coal-fired steam plants was investigated (18). The watershed, which is on the ERDA reservation at Oak Ridge, is within 20 km of three coal-fired steam plants, two in the TVA system and one belonging to ERDA. In conjunction with this program, there is an ongoing, well instrumented program monitoring a forested catchment (located within 15 km of two large coal-fired power plants). Measurements of selected trace contaminants in air, rain, on leaf surfaces and in stream water are made on a basis designed to elucidate transport, deposition, and cycling of these contaminants on the landscape (18, 30).

Yet these two studies, and others like them, highlight a number of problems. Uniform sampling methods were not employed, nor were methods of analysis of the samples documented. A computer simulation model was made of the trace metal flow around the Allen Steam Plant and compared with the measured data. Results were inconclusive (66), and the modeling and monitoring computer program did not interface with the SAROAD system used by EPA to monitor emissions.

In summary, the contribution from SCCP's to the trace metal mix in the environment is largely undetermined. In those spotty instances where studies have been made, for either specific locales or certain trace metals, no general conclusions may be drawn. That is, in certain cases the SCCP contribution is dominant, as selenium around the Allen Steam Plant (58). While in other cases, such as rural areas with high dust levels or for total copper emissions (56), the SCCP contribution is small to insignificant. In most cases, even the approximate contribution of a specific SCCP is unresolvable. But the chief reason for the incompleteness of the data is not primarily anthropogenic. Rather, it is the constraints imposed by available technology and costs, coupled with the sheer magnitude of the task, that have led to the current status.

2.4 RESEARCH NEEDS

The National Aerometric Data Bank (NADB) has provided a good beginning to assess the atmospheric trace metal levels. However their data are uneven and not of sufficient quantity to sketch out national or regional isopleths for each element. The regional and state offices have more data, but much of it is unpublished. Also, locally sponsored programs sometimes produce data of variable quality. More monitoring stations reporting trace metal information into the SAROAD system would be very desirable.

The evolution of such data may be forthcoming. With lead being declared a criteria pollutant in October 1978 (38), and State Implementation Plans due in July of 1979 for compliance by October of 1982, states will have to establish a lead monitoring network. With the task of HiVol atmospheric sampling being done and the catches analyzed for lead, small additional effort would produce data for other trace metals. This is particularly true with the newly developed multi-element analytical instruments beginning to proliferate (X-ray fluorescence, SSMS/ID and plasma fluorescence; see Section 8). More analysis and interpretation of the data would be highly beneficial. Interpretive reports such as those by Gordon and Zoller (46) and Hall et al. (67) are needed as much as more trace metal data.

The number of trace metal studies on water and soil are expected to increase with improving technology, and more and better data will be produced; however, local factors remain so variable and influential that only studies restricted to a locale for specific reasons appear to be warranted at this time.

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SECTION 3

TRACE METALS IN FUELS

The most influential factor in trace metal emissions from SCCP's is, of course, the fuel. "What goes in must come out," is a self-evident statement. Various design alternatives can do no more than shift the burden of trace metal emissions from one stream to another. Such tradeoffs are frequently desirable and usually the object of control technology design. How various designs influence the ultimate fate of trace metals is treated in Sections 4 and 5. In this section, the concentrations of trace metals in different source fuels will be reviewed, and the influence of the fuel characteristics on the destiny of trace metals will be discussed.

3.1 COAL

The most extensively analyzed and reported fuel source is coal. Most trace metal analyses of coals are carried out for one of four reasons: (1) to determine the trace metal concentrations and add to the building nationwide database; frequently this will cover a wide variety of coals; (2) as part of a study of one particular power plant to determine the fate of trace metals during the combustion and clean-up processes; this analysis will usually be only for the single coal used during the testing; (3) to determine the concentration, partitioning and behavior of one or two specific elements in the combustion process; while a variety of coals may be analyzed, only the element(s) of interest is considered; and (4) to determine the accuracy of a certain analytical procedure; the emphasis here is on comparing analytical techniques and the trace metal concentrations are usually given incidentally for a few different, often non-identified coals. The first class of analyses is the most useful for providing an understanding of the fuel source problems and alternatives; however, the method of reporting is not consistent. Frequently the reports are given in terms of major, minor and trace element concentrations (see Section 1, Introduction, for definition of these terms). Less extensive efforts result in only proximate or ultimate analysis. Many authors report the Btu value as part of the analysis, but the seldom reported trace element per Btu ultimately may be the most useful format (1). The most common unit remains percent by weight, usually in ppm for trace elements.

3.1.1 Whole Coals by Region

Since coals found in a local region are frequently similar, many data bases break up United States coal fields into geographical classes; for example, Eastern, Mid-continent, and Western. In general, Eastern coals are high sulfur, high Btu and low ash (anthracite and bituminous) whereas Western coals are often low sulfur, low Btu and high ash (subbituminous and lignite). Mid-continent coals are usually intermediate in these qualities. Anthracite coals are generally defined by percent of fixed carbon (about 86% or greater); some bituminous coals are also judged by their fixed carbon (between 69% or 86%), while others are judged by their caloric content (about 11,500 Btu/lb or greater). Subbituminous (8,300-11,500 Btu/lb) and lignite (less than 8,300 Btu/lb) are usually defined strictly by their caloric content. Most often, moisture and Btu values are reported on an "as received" basis. All other properties are referred to as a "dry" basis.

Tables 3-1, 3-2 and 3-3 list the trace element concentrations found in whole coal (contrasted with coal ash) for Eastern, Mid-Continent (Illinois Basin) and Western coals; they are representative of other data compilations for whole U.S. coals (2); also see references (3-7).

Although they are lowest in ash (the bulk of which is aluminosilicates), Eastern coals are generally highest in trace metal concentrations. Mid-continent coals are intermediate and Western coals are lowest in trace metals despite their higher overall ash content. In general, however, the variations are not large (less than X3). Exceptions include: (1) Western coals are highest in Ba, P, Sr, Ca, Na and (2) Illinois Basin coals (typical of Mid-Continent coals are highest in B, Be, Br, Cd, Ge, Mn, Ni, Pb,

TABLE 3-1. MEAN ANALYTICAL VALUES FOR 23 WHOLE COAL SAMPLES FROM THE EASTERN UNITED STATES
(Appalachian Coal Fields)

Element	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Standard Deviation	Number Samples
Ag	0.02 ppm	0.02 ppm	0.01	0.06	0.01	13
As	25 ppm	15 ppm	0.8	100	27	23
B	42 ppm	28 ppm	5.0	120	32	23
Ba	200 ppm	170 ppm	72	420	110	14
Be	1.3 ppm	1.1 ppm	0.23	2.6	0.56	23
Br	12 ppm	8.9 ppm	0.71	26	7.6	23
Cd	0.24 ppm	0.19 ppm	0.10	0.60	0.18	23
Ce	25 ppm	23 ppm	11	42	9.1	14
Co	9.8 ppm	7.6 ppm	1.5	33	7.8	23
Cr	20 ppm	18 ppm	10	90	16	23
Cs	2.0 ppm	1.6 ppm	0.40	6.2	1.6	14
Cu	18 ppm	16 ppm	5.1	30	7.3	23
Dy	2.3 ppm	2.0 ppm	0.74	3.5	0.94	14
Eu	0.52 ppm	0.47 ppm	0.16	0.92	0.22	14
F	89 ppm	84 ppm	50	150	31	23
Ga	5.7 ppm	5.2 ppm	2.9	11	2.6	23
Ge	1.6 ppm	0.87 ppm	0.10	6.0	1.7	23
Hf	1.2 ppm	1.1 ppm	0.58	2.2	0.45	14
Hg	0.20 ppm	0.17 ppm	0.05	0.47	0.12	23
I	1.7 ppm	1.4 ppm	0.33	4.9	1.1	14
In	0.23 ppm	0.22 ppm	0.13	0.37	0.08	14
La	15 ppm	14 ppm	6.1	23	5.3	14
Lu	0.22 ppm	0.18 ppm	0.04	0.40	0.12	14
Mn	18 ppm	12 ppm	2.4	61	16	23
Mo	4.6 ppm	1.8 ppm	0.10	22	6.3	23
Ni	15 ppm	14 ppm	6.3	28	5.7	23
P	150 ppm	81 ppm	15	1500	300	23
Pb	5.9 ppm	4.7 ppm	1.0	18	4.0	23
Rb	22 ppm	19 ppm	9.0	63	15	14
Sb	1.6 ppm	1.1 ppm	0.25	7.7	1.7	23
Sc	5.1 ppm	4.5 ppm	1.6	9.3	2.4	14
Se	4.0 ppm	3.4 ppm	1.1	8.1	2.0	23
Sm	2.6 ppm	2.4 ppm	0.87	4.3	1.0	14
Sn	2.0 ppm	0.97 ppm	0.20	8.0	2.4	19
Sr	130 ppm	100 ppm	28	550	130	14
Ta	0.33 ppm	0.26 ppm	0.12	1.1	0.28	14
Tb	0.34 ppm	0.28 ppm	0.06	0.63	0.17	14
Th	4.5 ppm	4.0 ppm	1.8	9.0	2.1	14
U	1.5 ppm	1.3 ppm	0.40	2.9	0.73	14
V	38 ppm	35 ppm	14	73	14	23
W	0.69 ppm	0.62 ppm	0.22	1.2	0.31	14
Yb	0.83 ppm	0.73 ppm	0.18	1.4	0.35	14
Zn	25 ppm	19 ppm	2.0	120	24	23
Zr	45 ppm	41 ppm	8.0	88	18	19
Al	1.7 %	1.6 %	1.1	3.1	0.56	23
Ca	0.47 %	0.34 %	0.09	2.6	0.51	23
Cl	0.17 %	0.10 %	0.01	0.80	0.21	23
Fe	1.5 %	1.3 %	0.50	2.6	0.69	23
K	0.25 %	0.21 %	0.06	0.68	0.14	23
Mg	0.06 %	0.05 %	0.02	0.15	0.03	23
Na	0.04 %	0.03 %	0.01	0.08	0.02	23
Si	2.8 %	2.6 %	1.0	6.3	1.1	23
Ti	0.09 %	0.09 %	0.05	0.16	0.04	23
Adl	1.2 %	0.99 %	0.50	4.0	0.89	14
Mois	2.7 %	2.4 %	1.0	6.8	1.5	23
Vol	33 %	32 %	17	42	8.0	23
FixC	55 %	54 %	45	72	7.2	23
Ash	12 %	12 %	6.1	25	4.3	23
Btu/lb	13111	13093	11374	13816	696	14
C	72 %	72 %	63	80	5.3	22
H	4.9 %	4.9 %	4.0	6.0	0.44	22
N	1.3 %	1.3 %	0.94	1.8	0.27	22
O	8.0 %	7.0 %	2.5	18	4.3	22
Hta	12 %	12 %	6.2	25	4.3	23
Lta	15 %	15 %	7.6	28	4.9	23
OrS	0.92 %	0.82 %	0.35	2.5	0.48	23
PyS	1.3 %	0.81 %	0.04	2.6	0.91	23
SuS	0.10 %	0.06 %	0.01	0.42	0.10	22
ToS	2.3 %	1.9 %	0.55	5.0	1.3	23
Sxrf	2.1 %	1.8 %	0.74	4.8	1.1	23

SOURCE: (2) See Table 3-4 for explanation of abbreviations.

TABLE 3-2. MEAN ANALYTICAL VALUES FOR 114 MID-CONTINENT WHOLE COAL SAMPLES
(From the Illinois Basin Coal Field)

Element	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Standard Deviation	Number Samples
Ag	0.03 ppm	0.03 ppm	0.02	0.08	0.02	37
As	14 ppm	7.4 ppm	1.0	120	20	113
B	110 ppm	98 ppm	12	230	50	99
Ba	100 ppm	75 ppm	5.0	750	110	56
Be	1.7 ppm	1.6 ppm	0.5	4.0	0.82	113
Br	13 ppm	10 ppm	0.6	52	7.4	113
Cd	2.2 ppm	0.59 ppm	0.1	65	7.4	93
Ce	14 ppm	12 ppm	4.4	46	7.5	56
Co	7.3 ppm	6.0 ppm	2.0	34	5.3	113
Cr	18 ppm	16 ppm	4.0	60	9.7	113
Cs	1.4 ppm	1.2 ppm	0.5	3.6	0.73	56
Cu	14 ppm	13 ppm	5.0	44	6.6	113
Dy	1.1 ppm	1.0 ppm	0.5	3.3	0.42	56
Eu	0.26 ppm	0.25 ppm	0.1	0.87	0.12	56
F	67 ppm	63 ppm	29	140	26	113
Ga	3.2 ppm	3.0 ppm	0.8	10	1.2	113
Ge	6.9 ppm	4.8 ppm	1.0	43	6.4	113
Hf	0.54 ppm	0.49 ppm	0.13	1.5	0.25	56
Hg	0.2 ppm	0.16 ppm	0.03	1.6	0.19	113
I	1.7 ppm	1.2 ppm	0.24	14	2.0	56
In	0.16 ppm	0.13 ppm	0.01	0.63	0.11	56
La	6.8 ppm	6.4 ppm	2.7	20	2.8	56
Lu	0.09 ppm	0.08 ppm	0.02	0.44	0.06	56
Mn	53 ppm	40 ppm	6.0	210	41	113
Mo	8.1 ppm	6.2 ppm	0.3	29	5.4	111
Ni	21 ppm	19 ppm	7.6	68	10	113
P	64 ppm	45 ppm	10	340	60	113
Pb	32 ppm	15 ppm	0.8	220	42	113
Rb	19 ppm	17 ppm	2.0	46	9.9	56
Sb	1.3 ppm	0.81 ppm	0.1	8.9	1.4	113
Sc	2.7 ppm	2.5 ppm	1.2	7.7	1.1	56
Se	2.2 ppm	2.0 ppm	0.4	7.7	1.0	113
Sm	1.2 ppm	1.1 ppm	0.4	3.8	0.55	56
Sn	3.8 ppm	0.94 ppm	0.2	51	6.8	60
Sr	35 ppm	30 ppm	10	130	23	56
Ta	0.15 ppm	0.14 ppm	0.07	0.3	0.06	56
Tb	0.22 ppm	0.18 ppm	0.04	0.65	0.14	41
Th	2.1 ppm	1.9 ppm	0.71	5.1	0.87	56
Tl	0.66 ppm	0.59 ppm	0.12	1.3	0.31	25
U	1.5 ppm	1.3 ppm	0.31	4.6	0.93	56
V	32 ppm	29 ppm	11	90	13	113
W	0.82 ppm	0.63 ppm	0.04	4.2	0.69	56
Yb	0.56 ppm	0.53 ppm	0.27	1.5	0.21	56
Zn	250 ppm	87 ppm	10	5300	650	113
Zr	47 ppm	41 ppm	12	130	27	88
Al	1.2 %	1.2 %	0.43	3.0	0.39	113
Ca	0.67 %	0.51 %	0.01	2.7	0.48	113
Cl	0.14 %	0.08 %	0.01	0.54	0.13	113
Fe	2.0 %	1.9 %	0.45	4.1	0.63	113
K	0.17 %	0.16 %	0.04	0.56	0.07	113
Mg	0.05 %	0.05 %	0.01	0.17	0.02	113
Na	0.05 %	0.03 %		0.2	0.04	113
Si	2.4 %	2.3 %	0.58	4.7	0.7	113
Ti	0.06 %	0.06 %	0.02	0.15	0.02	113
Adl	7.3 %	6.4 %	1.4	17	3.4	98
Mois	9.4 %	8.1 %	0.5	18	4.3	112
Vol	40 %	40 %	27	46	3.1	111
FixC	49 %	49 %	41	61	3.6	111
Ash	11 %	11 %	4.6	20	2.3	112
Btu/lb	12712	12702	11562	14362	470	107
C	70 %	70 %	62	80	3.0	110
H	5.0 %	5.0 %	4.2	6.0	0.31	110
N	1.3 %	1.3 %	0.93	1.8	0.19	110
O	8.2 %	8.0 %	4.2	14	1.8	109
Hta	11 %	11 %	3.3	20	2.5	112
Lta	15 %	15 %	3.8	24	3.3	112
OrS	1.6 %	1.4 %	0.37	3.2	0.6	112
PyS	2.0 %	1.8 %	0.29	4.6	0.78	111
SuS	0.1 %	0.05 %	0.01	1.1	0.16	109
Tos	3.6 %	3.4 %	0.56	6.4	1.1	113
Sxrf	3.4 %	3.2 %	0.79	6.5	1.1	112

SOURCE: (2) See Table 3-4 for explanation of abbreviations.

TABLE 3-3. MEAN ANALYTICAL VALUES FOR 28 WHOLE COAL SAMPLES FROM THE WESTERN UNITED STATES

Element	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Standard Deviation	Number Samples
Ag	0.03 ppm	0.02 ppm	0.01	0.07	0.02	22
As	2.3 ppm	1.5 ppm	0.34	9.8	2.6	29
B	56 ppm	48 ppm	16	140	32	27
Ba	500 ppm	430 ppm	160	1600	320	22
Be	0.46 ppm	0.35 ppm	0.10	1.4	0.34	29
Br	4.7 ppm	2.1 ppm	0.50	25	7.3	29
Cd	0.18 ppm	0.15 ppm	0.10	0.60	0.13	29
Ce	11 ppm	9.1 ppm	2.8	30	8.0	22
Co	1.8 ppm	1.5 ppm	0.60	7.0	1.5	29
Cr	9.0 ppm	8.1 ppm	2.4	20	4.2	29
Cs	0.42 ppm	0.16 ppm	0.02	3.8	0.82	22
Cu	10 ppm	8.5 ppm	3.1	23	5.9	29
Dy	0.63 ppm	0.57 ppm	0.22	1.4	0.32	22
Eu	0.20 ppm	0.16 ppm	0.07	0.60	0.17	22
F	62 ppm	57 ppm	19	140	28	29
Ga	2.5 ppm	2.1 ppm	0.80	6.5	1.4	29
Ge	0.91 ppm	0.50 ppm	0.10	3.0	0.92	29
Hf	0.78 ppm	0.70 ppm	0.26	1.3	0.33	22
Hg	0.09 ppm	0.07 ppm	0.02	0.63	0.11	29
I	0.52 ppm	0.46 ppm	0.20	1.0	0.25	22
In	0.10 ppm	0.07 ppm	0.01	0.25	0.07	22
La	5.2 ppm	4.5 ppm	1.8	13	3.0	22
Lu	0.07 ppm	0.05 ppm	0.01	0.43	0.09	22
Mn	49 ppm	28 ppm	1.4	220	49	29
Mo	2.1 ppm	0.59 ppm	0.10	30	5.6	29
Ni	5.0 ppm	4.4 ppm	1.5	18	3.2	29
P	130 ppm	82 ppm	10	510	130	29
Pb	3.4 ppm	2.6 ppm	0.70	9.0	2.3	29
Rb	4.6 ppm	2.4 ppm	0.30	29	6.6	22
Sb	0.58 ppm	0.45 ppm	0.18	3.5	0.61	29
Sc	1.8 ppm	1.5 ppm	0.50	4.5	1.1	22
Se	1.4 ppm	1.3 ppm	0.40	2.7	0.59	29
Sm	0.61 ppm	0.56 ppm	0.22	1.4	0.29	21
Sn	1.9 ppm	0.43 ppm	0.10	15	3.8	26
Sr	260 ppm	220 ppm	93	500	140	22
Ta	0.15 ppm	0.12 ppm	0.04	0.33	0.08	22
Tb	0.21 ppm	0.17 ppm	0.06	0.58	0.15	18
Th	2.3 ppm	1.8 ppm	0.62	5.7	1.5	22
U	1.2 ppm	0.99 ppm	0.30	2.5	0.65	22
V	14 ppm	12 ppm	4.8	43	10	29
W	0.75 ppm	0.58 ppm	0.13	3.3	0.65	22
Yb	0.38 ppm	0.34 ppm	0.13	0.78	0.17	22
Zn	7.0 ppm	5.0 ppm	0.30	17	4.9	29
Zr	33 ppm	26 ppm	12	170	31	26
Al	1.0 %	0.88 %	0.31	2.2	0.56	29
Ca	1.7 %	1.5 %	0.44	3.8	0.93	29
Cl	0.03 %	0.02 %	0.01	0.13	0.03	29
Fe	0.53 %	0.49 %	0.30	1.2	0.24	29
K	0.05 %	0.03 %	0.01	0.32	0.06	29
Mg	0.14 %	0.12 %	0.03	0.39	0.09	29
Na	0.14 %	0.06 %	0.01	0.60	0.16	29
Si	1.7 %	1.3 %	0.38	4.7	1.2	29
Ti	0.05 %	0.05 %	0.02	0.13	0.02	29
Adl	14 %	12 %	4.5	31	7.3	21
Mois	18 %	16 %	4.1	37	8.9	29
Vol	44 %	44 %	33	53	3.8	29
FixC	46 %	46 %	35	55	5.3	29
Ash	9.6 %	8.9 %	4.1	20	3.7	29
Btu/lb	11409	11377	10084	12901	872	22
C	67 %	67 %	58	74	4.2	29
H	4.7 %	4.6 %	3.8	5.8	0.48	29
N	1.0 %	0.98 %	0.59	1.5	0.22	29
O	17 %	17 %	8.8	22	3.2	29
Hta	9.6 %	8.9 %	4.1	20	3.7	29
Lta	12 %	11 %	4.7	26	5.1	29
OrS	0.53 %	0.50 %	0.25	1.1	0.19	29
PyS	0.19 %	0.10 %	0.01	1.2	0.24	29
SuS	0.04 %	0.03 %	0.01	0.22	0.04	27
ToS	0.76 %	0.70 %	0.34	1.9	0.33	29
Sxrf	0.73 %	0.70 %	0.40	1.2	0.20	29

SOURCE: (2) See table 3-4 for explanation of abbreviations

TABLE 3-4. EXPLANATION OF ABBREVIATIONS USED IN TABLES 3-1, 3-2, AND 3-3

Adl	Air-dry loss
FixC	Fixed Carbon
Hta	High Temperature Ash
Lta	Low Temperature Ash
Mois	Moisture, as received
OrS	Organic sulfur
PyS	Pyritic sulfur
SuS	Sulfate sulfur
Sxrf	Sulfur by X-Ray Fluorescence
ToS	Total sulfur
Vol	Volatile matter

Zn, Fe, and S. Finally, only four elements in coals significantly exceed the average crustal abundance: boron, chlorine, selenium and arsenic.

3.1.2 Elemental Composition in Ashed Coal

More frequently, especially in the past, analyses have been done on "ashed" coal rather than on whole coal. In this procedure the coal is burned in an oven, and the resulting ash is digested in acid and analyzed. This procedure, high-temperature ashing at about 750°C, assumes that metal oxides compose the ash, but the method is not able to analyze for the volatile elements: Hg, Se, Be, F, As and sometimes Pb. Recently, several methods have been developed to overcome this difficulty. Low-temperature ashing (150°C), using ozone or oxygen radicals to "burn" the coal, has been one approach. Another approach has been to trap and analyze the off-gases from high-temperature ashing. Neutron analysis methods require no sample preparation and can accurately measure the concentration of the volatile elements in the whole coal. Ruch et al. (5-7) have evaluated the accuracy of elemental determinations for volatile elements, reporting trace elemental concentrations for a large number of whole coals and their ashes. Also see Lee et al. (8), Pollock (9) and Cowherd et al. (10) for similar studies. Hence, concentrations for these volatile elements, especially in older analytical data, reflect a degree of uncertainty. Ashing remains as the most common method of analysis for trace metals in coals, and much of the elemental data for coal are presented as ash concentrations.

Although certain regions are higher in trace elements, an overview shows that most U.S. coals contain similar amounts of total trace elements in a coal ash (about 0.65% in ash), however, large variations may occur for each element. Following Ctvrtnicek et al. (11), Table 3-5 shows that barium, strontium and zirconium levels are higher in Western ashes; boron, germanium, lead and zinc are highest in Mid-continent ashes; and Eastern ash is noticeably higher in copper and lithium. Cadmium, mercury and selenium are not usually included because of their volatility; approximate values based on Western coal are (in ppm): Cd, 0.1-0.8; Hg, 0.1-0.2;

TABLE 3-5. AVERAGE TRACE ELEMENT CONTENT IN ASH OF COAL FROM THREE AREAS, AS WEIGHT PERCENT[a]

Element	Crustal abundance (13)	Approximate lower limit of detection (14)	Eastern Province		Interior Province		Western States	
			Frequency of detection	Average trace element content of ash	Frequency of detection	Average trace element content of ash	Frequency of detection	Average trace element content of ash
Barium	0.0425	0.002	100	0.0876	100	0.0399	100	0.1467
Beryllium	.00028	.0001	100	.0012	100	.0014	100	.0006
Boron	.0010	.002	100	.0255	100	.0731	100	.0529
Chromium	.0100	.0001	100	.0230	100	.0224	100	.0066
Cobalt	.0025	.0020	100	.0184	98	.0193	98	.0097
Copper	.0055	.0001	100	.0128	100	.0089	100	.0047
Gallium	.0015	.0002	100	.0071	100	.0039	100	.0033
Germanium	.00015	.0003	99	.0048	100	.0104	95	.0017
Lanthanum	.0030	.01	92	.0165	86	.0131	81	.0128
Lead	.0013	.0001	100	.0055	100	.0131	100	.0029
Lithium	.0020	.0001	100	.0584	100	.0235	100	.0168
Manganese	.0950	.0001	100	.0260	100	.0325	100	.0212
Molybdenum	.00015	.0001	99	.0082	99	.0073	100	.0020
Nickel	.0075	.0001	100	.0209	100	.0262	100	.0054
Scandium	.0022	.002	100	.0089	100	.0069	97	.0052
Strontium	.0375	.001	100	.1052	100	.0658	100	.1456
Tin	.0002	.0001	100	.0019	99	.0019	100	.0017
Vanadium	.0135	.0001	100	.0336	100	.0325	100	.0152
Ytterbium	.00034	.0001	100	.0007	100	.0005	100	.0003
Yttrium	.0033	.001	100	.0142	100	.0118	100	.0076
Zinc	.0070	.005	98	.0230	100	.0743	93	.0258
Zirconium	.0165	.005	100	.0704	100	.0825	100	.0850
Arsenic	.00018	.005	67	.0159 (.0107)	41	.0119 (.0049)	16	.0073 (.0012)
Bismuth	.00002	.0001	82	.0002 (.0002)	77	.0001 (.0001)	83	.0001 (.0001)
Cerium	.0060	.02	31	.0238 (.0074)	11	.0214 (.0024)	13	.0238 (.0031)
Neodymium	.0028	.01	29	.0213 (.0062)	10	.0183 (.0018)	15	.0295 (.0044)
Niobium (Columbium)	.0020	.001	73	.0053 (.0039)	88	.0055 (.0048)	85	.0053 (.0045)
Rubidium	.0090	.001	97	.0239 (.0232)	100	.0276 (.0276)	58	.0064 (.0037)
Thallium	.00005	.0005	43	.0019 (.0008)	49	.0008 (.0004)	9	.0005 (.00005)
Average Trace Element, % of Ash				.6651		.6568		.6466
Average Ash, % of Dry Coal				9.3		10.5		9.8
Average Trace Element, % of Dry Coal				.0618		.0690		.0634
Number of Samples				600		123		104

[a] Average calculated for number of samples in which element was detected, except that averages in parentheses were calculated for all of the samples tested using zero for element contents below limit of detection.

SOURCE: (11)

Se, 0.5-5.0. They also reported that no correlation could be found (for Western coals) relating the percent of ash in coal to the individual or total trace metal content.

Altschuler (12) has recently (1978) reported on the distribution and nature of about four trillion tons of coal. While his main interest was sulfur, he does comment on the trace metals content. He notes that certain elements in coal are enriched over crustal abundances, and those elements are commonly associated with organic fixation or sulfides. Of the ten elements most enriched in coals, nine of them are potentially hazardous to humans or the environment: Sb, As, Be, Cd, Pb, Mo, Se, S, and U.

Ray and Parker (15) give tables of coal ash analyses for various U.S. coals broken down by type; i.e., anthracite, volatile bituminous, etc. Wewerks *et al*. (16) also gives tables of both whole coals and coal ash broken into coal types (or rank). Table 3-6 gives ranges of elements found in U.S. coals and coal ashes. Table 3-7 is another author's compilation of similar data for comparison (17); this table in addition gives the average values of trace elements and the percent of each element found in the resulting fly ash.

There are numerous publications giving analytical trace element data for specific coal fields, coal seams or regional and area coals; many are included in the bibliography accompanying this report. Recently, an extensive compilation of U.S. coal data has been gathered together and stored in a computerized database at Pennsylvania State University. This database includes all types of data available for coal: whole coal, low temperature ash, ultimate and proximate analysis, etc. It is organized by county, and the data are specific to each seam. The information is readily available for a nominal fee associated with the service (18).

Many other articles exist that have reviewed or summarized data on trace element in coal. Work done before 1970 is likely to be imprecise or inaccurate owing to the poorer technology of the times and the (then) lack of a coal standard. Some frequently cited and useful papers on elemental analysis not referred to elsewhere include: (19-24).

TABLE 3-6. RANGE OF TRACE ELEMENTS IN U.S. COALS AND ASHES

Element (Major)	Whole Coal (%)	Coal Ash (%)
Na	0-0.20	0.71-2.72
Mg	0.1-0.25	0 -2.4
Al	0.43-3.04	5.3-21.2
Si	0.58-6.09	9.3-28
Cl	0-0.56	-
K	0.02-0.43	0.66-1.32
Ca	0.05-2.67	0.58-14
Ti	0.002-0.32	0.1-2.6
Fe	0.32-4.32	2.09-24.4
Zn	0-0.56	0-1.6
Sr	-	0.009-0.96
Ba	-	0.01-1.39
(Minor)	(ppm)	(ppm)
Li	-	<20-3100
Be	0-31	0-1100
B	1.2-356	30-6500
F	10-295	-
P	5-1430	<440-3360
Sc	10-100	2-155
V	0-1281	6-3800
Cr	0-610	<1-1800
Mn	6-181	30-1800
Co	0-43	0-600
Ni	0.4-104	0-1200
Cu	1.8-185	10-[illegible]
Ga	0-61	0-540
Ge	0-819	0-1500
As	0.5-106	21-570
Se	0.4-8	-
Br	4-52	-
Rb	-	<91-1100
y	<0.1-59	0-620
Zr	8-133	100-1450
Mo	0-73	0-2900
Ag	-	<1-84
Cd	0.1-65	-
Sn	0-51	0-4250
Sb	0.2-9	<40-230
La	0-98	0-820
Yb	-	<2-23
W	-	<10-182
Hg	0.01-1.6	<70-259
Pb	4-218	10-1420
Bi	-	1-900
U	<10-1000	-

SOURCE: (16)

TABLE 3-7. TRACE METALS IN COAL AND FLY ASH

Element	Average Concen. in Coal (ppm)	Concen. Range in Coal (ppm)	Concen. Remaining in Fly Ash (ppm)	% Remaining in Fly Ash after Combustion at 500°C
Ag	-	0.1-2	0.4-3	790
As	5	0.5-93	2.8-200	35-50
B	55	5-224	-	795
Ba	64	2-500	110-700	-
Be	2	0.2-4	1-7	82
Cd	-	0.1-65	2-100	38
Co	12	1-43	25-70	790
Cr	20	4-54	80-500	795
Cu	12	5-61	33-300	795
F	-	25-220	10-100	-
Fe	-	1800-8000	-	790
Ge	8	1-43	-	795
Hg	2	0.2-5	0.1-18	0-10
In	0.18	-	0.2	-
Mn	30	6-181	150-500	795
Mo	6	1-30	34	67
Ni	20	3-80	45-300	76
Pb	9	4-218	95-440	37
Ra	-	-	-	-
Rb	25	-	180	790
Sb	-	0.2-8.9	5.6-100	50
Sc	8	-	29.5	790
Se	3	0.45-7.7	0.77-40	24
Sn	2	1-51	1.9-100	795
Sr	85	46-160	69-1000	-
Te	0.5	-	-	36
Th	3.47	-	17.1	790
Tl	0.125	<0.2-0.7	5-76	-
U	-	10-160	-	-
V	33	11-78	180-2000	70
W	0.93	-	2.7	790
Zn	329	6-5350	70-1000	795

SOURCE: (17)

3.1.3 Elemental Forms in Coal

The widespread geographical trends of trace metals in coals discussed above are not intended to give specific details. Local geological factors more frequently influence the concentrations of trace metals. Hall, Magee, and Varga (25-27) have reported that certain elements tend to be concentrated near the edges of a coal seam (Ge, Be, Ga, B); other elements may be enriched if the seam is close to an ore deposit (Mo, Sn, Pb, Hg, Cl being typical examples). But their basic conclusion was that only a few trace metals vary appreciably depending upon geography, and that elemental concentrations in coal are near their average crustal abundance (their Clarke values). That is, most trace elements are between 1-100 ppm in all regions, with some 20 trace metals generally between 5-10 ppm. Boron and fluoride are usually higher, mercury, commonly lower. Concentrations near crustal abundances are not considered toxic. Hall et al. (25) also reported, as did Altschuler (12), that those elements that are concentrated in coals and whose concentrations fluctuate most widely have generally been associated with the organic phase (S, Ge, Be, B, Ga).

Gluskoter (28) has addressed the form of trace metals in coal. He has used density separations to define the organic (lighter) and inorganic (denser) phases of the coal. The fractions were then analyzed for comparative amounts of trace metals. He defined four groups: strong organic affinity (Ge, Be, B); organic association (P, Ga, Sb, Ti, V); inorganic association (Co, Ni, Cr, Se, Cu); strong inorganic affinity (Hg, Zr, Zn, As, Cd, Pb, Nm, Mo). There are exceptions to these classes for individual coal samples, but other workers are in general agreement. Gluskoter reports that Horton and Aubrey (29), using a similar technique, concluded Be, Ge, Va, Ti, and B were largely organically combined in coal, while P, Mn and Sn were inorganically combined. Zubovic (30) has compiled a list based on percentage or organic affinity: Ge (87), Be (82), Ga (79), Ti (78), B (77), V (76), Ni (59), Cr (55), Co (53), Y (53), Mo (40), Cu (34), Sn (27), La (3), Zn (0). And he concluded that this series was related to the chelating properties of the metals. The fate of a trace metal during combustion is believed to be partially influenced by its degree of organic association; see Section 3.4.

Gluskoter (28) and others have further studied the chemical form of trace metals in the inorganic phase of coal. They state that the overwhelming majority of the minerals in coal are in one of four groups:

- Aluminosilicates, or clay minerals, are most abundant Most common among them are illite $[(OH)_4K_2(Si_6 \cdot Al_2)Al_4O_{20}]$ and kaolinite $[(OH)_8Si_4Al_4O_{10}]$. About 52% of Illinois Basin inorganic material are aluminosilicates.
- Sulfides and sulfates show a considerable range of variation. Pyrite is the dominant sulfide mineral in coal; marcasite is also common. These are different crystal forms of FeS. Significant amounts of sphalerite (ZnS) and galena (PbS) are also found in coals. Sulfates are not common and are often absent in unweathered coal. When found, they are most commonly an iron sulfate. About 25% of Illinois Basin inorganic materials are sulfur minerals.
- Carbonates vary widely in composition. Frequently reported forms are calcite ($CaCO_3$), siderite ($FeCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$) and ankerite ($2CaCO_3 \cdot MgCO_3 \cdot FeCO_3$). These carbonates make up about 9% of Illinois Basin inorganic matter.
- Silica, or quartz, is found in all coals. For Illinois Basin samples, silica represents about 15% of all minerals. Quartz is the only mineral of those mentioned that is stable and persists in high-temperature ashing at 750°C.

Gluskoter further reports that Goldschmidt (31) has classified elements on their affinities to occur in certain mineralogical groups. The chalcophile elements commonly form sulfides (Zn, Cd, Hg, Cu, Pb, As, Sb, Se, and others). The lithophile elements generally occur in the silicate phases (Si, Al, Ti, K, Na, Zr, Be, Y). Mg, Fe and Mn are usually associated with the carbonates. The mineral form of the trace metal will have an effect on its fate during preprocessing and combustion; see Sections 3-3 and 3-4.

Miller (32) has looked for correlations of trace metals with mineral types. He studied 15 Illinois coals, and the elements for which he found correlation coefficients greater than 0.5 are given in Table 3-8; also see (4).

TABLE 3-8. TRACE ELEMENTS, MINERAL CORRELATIONS[1]

As, Be, Cu, Sb	Pyrite
B, Cd, Zn, Hg	Sphalerite
B, Cd, Mn, Se, Mo, V	Calcite
B, Cr, Mn, Cd, Mo, Se, V, Zn	Quartz
B, Cu, F, Hg, Sn, V	Clays

[1] Correlation coefficient >0.5

SOURCE: (32)

3.1.4 Incidentally Reported Elemental Studies in Coals

Another body of data on fuel source concentrations is associated with studies in which trace element pathways through power plants were studied. This type of research usually involves measuring the total amount of each element entering the process and the total leaving in each effluent stream. This necessarily involves a trace metal analysis of the fuel. The data are specific to the fuel being used at the time of the study. Section 5 reports complete details on a number of these studies.

Lyon (35), in a recent book, has summarized most aspects of a three year study of the Allen Steam Plant in Memphis, Tennessee. This study, which was funded through Oak Ridge National Laboratory, generated many papers. Included in this work were several coal and coal ash analyses.

Ray and Parker (15) have reviewed several studies of trace metal partitioning; contained in this review are references to each study. They have reviewed work done at the following facilities:

- Illinois Power Plant (36),
- Midwestern Power Plant (37),
- Chalk Point Station (38-41),
- Valmont Power Station (42-44),
- Allen Steam Plant (35, 45-53),
- Canadian Steam Plant (54),
- three Northern Great Plains Plant (13, 14, 55-57), and
- Widows Creek Power Plant (10).

Other authors reporting source fuel, trace metal concentrations as part of a larger study include Block and Dams (58), Gasper and Dauzvardia (59), Cato (60), Fancher (61), Coutant et al. (62), Ondov et al. (63) and Ragaini and Ondov (64), Rancitelli (65), Wangen and Wienke (66).

In a similar vein, analysis of one or several coals have been reported in papers whose principal concern was the analytical methodology. Often the results of several labs are compared, and the NBS standards are frequently included. An explanation of the analytical techniques involved will be found in Section 8.3. A partial list of these primarily analytical studies which incidentally reported concentrations of trace metals in coals is given below, classified by analytical technique:

- Instrumental Neutron Activation Analysis (INAA) - (67-79),
- Atomic Absorption Spectrometry (AA) - (80-81),
- Mass Spectrometry:
  Spark source only - (82-86),
  With Isotope dilution - (87, 88),
- X-ray Fluorescence - (72, 73, 89-92), and
- Comparisons - (71-73, 81, 82, 93).

Babu (94), in reviewing all the major analytical techniques, reports several trace element analyses of various coals.

There are several articles that deal specifically with NBS standard trace metal coal sample. In 1973 von Lehmden et al. (72, 73), had several identical coal samples analyzed at about 50 different labs around the United States for trace metal content. The range of results was very broad, being greater than an order of magnitude for many elements. He thus demonstrated the need for a standard sample. NBS responded and by 1975, a comparative analysis of the NBS standard by four labs using INAA produced very similar results (71). Other works have continued to measure and confirm the trace metal concentration in the NBS coal standard (70, 95).

Another type of analysis, forcusing on one or two elements only, has also resulted in some trace metal information on fuels. This type of paper or book is frequently long and extensively treats many aspects of a particular element. Trace metals for which this approach has been used include:

mercury (96-100); lead (101-102); uranium and thorium (103); boron (104); cadmium (105); chromium (106); beryllium (107); lead and cadmium (108, 109); lead, chromium, cadmium, zinc, and mercury (110). Also, Babu (94) devotes a chapter in his book exclusively to mercury.

3.2 FUELS OTHER THAN COALS

By far, the vast majority of trace metal literature concerns coal, and with justification. Indeed, coals run from a few to thirty percent inorganic material, and that material contains roughly the crustal abundance of trace metals. When the coal is burned, these elements are released and, if they do not escape the facility, are concentrated in the ash. Oil on the other hand usually is less than 0.1 percent ash, and the trace metal environmental impact is generally believed to be less. Natural gas burns essentially without ash. It is worthy of note that urban refuse, with a total ash content comparable to coal, is remarkably free of sulfur.

3.2.1 Petroleum

The most abundant metals in oil are vanadium and nickel, but iron, zinc, chromium, copper, manganese and cobalt and others are almost always present in concentrations ranging from less than 1 ppb to more than 100 ppm (111). Other metals that have been identified in oils include: U, Zr, Sr, Sn, Pb, Nd, Mo, La, Ga, Ca, Ce, Ba, B, As, K, Na, Mg, Tl, Al (112). Table 3-9 gives typical trace metal concentrations values for several crude oils analyzed by neutron activation (113). Oil normally does contain some fine inorganic sediment; however, the trace metals do not seem to be associated with this phase. If the oil is filtered, the fine black filtrate deposits show no unusual levels of any trace metal (111).

The metals are usually associated with the liquid phase and believed to be chelated or complexed with ligands; however, the heavier oils typically have higher levels of trace metals that are concentrated in the asphaltenes. On the molecular level, V and Ni are usually classified either as metalloporphyrins or non-porphyrin Ni and V. Widely varying ratios of the two forms have been reported. This may be due in part to some metalloporphyrins being strongly associated with the asphalt phase (114).

TABLE 3-9. TRACE ELEMENT CONTENTS OF SOME CRUDE OILS BY NEUTRON ACTIVATION ANALYSIS

	CONCENTRATION IN CRUDE OIL (ppm)			
Element	California (Tertiary)	Libya	Venezuela (Boscan)	Alberta (Cretaceous)
V	7.5	8.2	1100.	0.682
Cl	1.47	1.81	--	25.5
I	--	--	--	1.36
S	9.90	4694.	--	1450.
Na	13.2	13.0	20.3	2.92
K	--	4.93	--	--
Mn	1.20	0.79	0.21	0.048
Cu	0.93	0.19	0.21	--
Ga	0.30	0.01	--	--
As	0.655	0.077	0.284	0.0024
Br	0.29	1.33	--	0.072
Mo	--	--	7.85	--
Cr	0.640	0.0023	0.430	--
Fe	68.9	4.94	4.77	0.696
Hg	23.1	--	0.027	0.084
Se	0.364	1.10	0.369	0.0094
Sb	0.056	0.055	0.303	--
Ni	98.4	49.1	117.	0.609
Co	13.5	0.032	0.178	0.0027
Zn	9.76	62.9	0.692	0.670
Sc	.0088	.0003	.0044	--
U	--	0.015	--	--

SOURCE: (113)

A book by Yen (115) has been published (1975) dealing with trace metals in petroleum. The reader is referred to that book and the references therein for a detailed exposition of the subject. The reader is also advised to see Mezey *et al*. (116) who treat the contaminants (including trace metals) in liquid fuels and their removal (117); that report draws heavily from Yen.

Given *et al*. (118) have looked at trace metal concentrations in a coal and compared them to the solids and oils resulting from catalytic hydrogenation of that coal. Titanium appears to be somewhat enriched in the oils relative to other elements. Also, Knauer and Milliman (119) have reported analyzing petroleum products to mercury. Finally, Goldstein and Siegmund (120) have looked at the influence of fuel oil composition on particulate mass loading and size distribution. While they do not explicitly deal with trace metals, many of their results have implications relevant to the understanding of trace metal behavior in fuels.

3.2.2 Urban Refuse

Urban refuse is growing in use as a fuel source, often combined with a fossil fuel. It has been estimated that by 1980, energy from refuse burning will be equivalent to 40,000 barrels of oil per day (121). The trace element content of urban refuse has been studied by a team at College Park Metallurgy Research Center at College Park, Maryland (Bureau of Mines support), and a series of papers have resulted (122-126). The following discussion draws largely on data developed by this group.

Urban refuse has a lower Btu content than coal, but it is also low in sulfur. The proximate analysis of refuse is compared with coal in Table 3-10. It should be noted that when discussing urban refuse as a fuel, one generally means processed refuse, or the combustible fraction thereof.

TABLE 3-10. PROXIMATE ANALYSIS OF COAL AND COMBUSTIBLE FRACTION OF URBAN REFUSE

	Coal	Refuse
Moisture, %	3.5-7.0	15-30
Ash, %	9-12	5-25
Volatile, %	35-40	30-60
Fixed Carbon, %	50-55	1-15
Btu/lb, as received	10,000-12,600	2,000-5,000
Btu/lb, dry	11,000-13,300	6,000-9,000
Sulfur, %	1-2.5	0.1-0.3
Chlorine, %	<0.1	0.3-1.5

Source: (122)

Chlorine is of interest in refuse because of the higher potential amounts introduced by plastics and chloride salts; however, the inorganic forms usually are high melting solids and remain in the bottom ash. While it is true that trace elements in refuse can vary widely depending upon its source, the elemental content is remarkably constant from one geographic region to another. Apparently mass production and distribution of consumer goods leads to a corresponding uniformity of refuse (125).

Table 3-11 lists minor and trace element concentrations for refuse, paper, magazines and coal. Prominant differences exist, and the presumed sources of the differences between coal and refuse include: aluminum (foil, food wrapping), chlorine (plastics, salts), silicon (sand, glass, clay), titanium and zinc (pigments). Silver, cadmium, chlorine, copper, mercury, lead, and zinc are an order of magnitude higher in the combustible fraction of urban refuse than in coal; titanium is also noticeably higher. Sulfur, conversely, is an order of magnitude less than in coal. The paper by Haynes et al. (125) gives the greatest exposition of data and analytical techniques of the series, and the reader is referred there for a more extensive breakdown and analysis of the data.

TABLE 3-11. CONCENTRATIONS OF ELEMENTS IN COAL, PAPER PRODUCTS AND THE COMBUSTIBLE FRACTION OF URBAN REFUSE (TYPICAL VALUES IN PARENTHESIS)

Major elements (conc. in pct)	Urban Refuse	Selected Paper Products	Magazines	Coal
Aluminum......	0.3-1.6 (1.1)	0.1-3.0 (1.0)	1.0-6.0	.1-2.0 (.14)
Calcium.......	.23-1.0 (0.5)	.04-2.7 (0.5)	.04-1.1	.007-.50 (.03)
Chlorine......	.3-1.5 (0.4)	.05-2.5 (0.1)	-	0-.1 (.01)
Iron..........	.05-.7 (0.2)	.01-.06 (.03)	.04-.5	.01-1.0 (0.1)
Magnesium.....	.05-.8 (0.1)	.002-.2 (.05)	.005-.3	.01-.4 (.02)
Phosphorous...	.001-.7 (0.1)	-	-	<.03
Potassium.....	.03-.2 (0.07)	.01-.10 (.03)	.01-.03	.01-.60 (0.2)
Silicon.......	1.-10 (4)	-	-	.08-4.1 (0.2)
Sodium........	.15-.9 (0.5)	.01-3.3 (0.3)	.01-.1	.01-.35 (0.2)
Sulfur........	.1-.3 (0.2)	<.3	-	1.-2.5 (1.2)
Titanium......	.07-1.7 (0.2)	.01-1.7 (1.0)	.3-1.8	.003-.18 (.006)
Zinc..........	.04-.8 (0.1)	.005-.02 (.008)	.001-.04	.001-.10 (.003)
Minor elements (conc. in ppm)				
Rare earths...	-	<600.	-	<50.
Antimony......	20-80 (45)	.02-250. (3)	-	1-1,800 (20)
Arsenic.......	<3	.001-9	-	1-70 (45)
Barium........	35-100 (50)	1-10,200 (1)	1-300	20-1,600 (80)
Beryllium.....	<2	<4	<2	.4-90 (25)
Bismuth.......	3-45 (22)	-	<15	.02-3 (0.2)
Boron.........	5-70 (15)	.1-20 (1)	-	1-270 (100)
Cadmium.......	3-70 (15)	.01-19 (0.3)	0-2	.2-5 (0.5)
Cesium........	<20	<35 (6)	-	.1-9 (0.3)
Chromium......	10-175 (30)	.4-330 (20)	70-260	.3-400 (1)
Cobalt........	2-17 (5)	1-4	10-20	.3-135 (25)
Copper........	30-450 (195)	.04-100 (12)	4-100	1-180 (7)
Germanium.....	<6	<15	-	.03-1,000 (45)
Gold..........	<2	.01-90 (.03)	-	.02-.5 (0.1)
Lead..........	110-1,300 (230)	.3-250 (10)	20-1,400	1-100 (7)
Lithium.......	2-10 (3)	2-200 (10)	5-15	1-165 (20)
Manganese.....	50-480 (85)	.5-500 (25)	1-50	20-240 (25)
Mercury.......	-	.1-90 (0.3)	-	.07-.6 (.15)
Molybdenum....	10-30 (20)	3-330	-	1-20 (5)
Nickel........	4-50 (15)	1-100 (5)	10-20	3-900 (65)
Niobium.......	<6	<15	-	3-40 (4)
Platinum......	<10	<35	-	<.06
Rubidium......	< 6	9-60	-	1-450 (25)
Scandium......	-	1-18 (1)	-	0-36 (6)
Silver........	.1-16 (2)	.03-6 (0.2)	<7	.01-8 (0.2)
Strontium.....	20-70 (50)	5-100 (30)	5-40	15-1,000 (135)
Tantalum......	<4	.15-200 (3)	-	<1 (6)
Tin...........	20-95 (50)	.1-20 (2)	<30	1-50 (20)
Tungsten......	<30	<70	-	.5-40 (20)
Vanadium......	5-70 (15)	.1-20 (10)	-	2-80 (20)
Zirconium.....	1-70 (10)	.05-25 (5)	-	25-450 (70)

Source: (122, 132)

There have been a number of articles on urban refuse incinerators, primarily involving auxiliary power generation. Of all the reports identified in this literature search, only the series cited above deals directly with trace metal analysis of refuse. The others are concerned with various aspects of particulate and pollution control, refuse-fossil fuel mixtures, fouling, safety, noise, aqueous pollutants or non-trace metal chemical composition of refuse (127-132); these reports relate to trace metal content only by inference. See Section 5.7 for a quantitative discussion of the emissions from urban refuse.

3.2.3 Wood

During the 1970's, there have been a smattering of articles analyzing the use of wood as an alternate fuel. They generally claim that wood has a greater Btu content per dollar than coal or oil. In certain areas of the country, wood could substantially reduce the reliance on other fuels. Use of timber scraps would also encourage growth in a logged area. However, none of these articles report any trace metal results, and the conspicuous absence of such data implies that they do not exist. For example see (133).

An EPA sponsored study by Battelle (Hall *et al*., 134) reported a comparison of wood and fossil fuels. This report probably represents the most definitive document available on wood used as fuel, including a brief discussion of trace metals in wood. Brown (135) has also studied the role of trace elements in wood combustion and published a table (reproduced in Hall, *et al*.) of trace metals in ashed wood. That data are included in Table 5-35 of this report. See Section 5.8 for a discussion of trace metals in emissions from wood.

3.3 COAL PREPROCESSING

In discussions on the form of trace metals in coal, the effects of precombustion preparation cannot be neglected. The principal objective of these procedures is to separate out as much of the mineral matter as possible before burning. This is done mechanically by exploiting the greater density of the non-organic phases. After grinding, much of the mineral matter is separated by differential settling or some form of centrifugation. This is usually done to a large extent at the mine site and results in large piles of primarily mineral debris called gob piles and culm banks. This crude processing, not occurring at the combustion site, is not to be considered as part of an SCCP process. However, finer grinding, sizing, and further separation is sometimes done at the plant site. The mineral debris generated at the site is usually combined with the combustion ash or disposed of in similar manner.

Effective preprocessing can considerably reduce the particulate loading and the potential atmospheric emissions. The pyrites, being quite dense (about 5 g/cc) and containing much of the sulfur, are usually the major components removed. Of course, other trace elements are removed as well, but in general, the details are poorly understood. Miller (32) has reported that the following elements in Illinois coals are reduced by more that 50% when 20% of the total raw coal is removed by float-sink separations: Al, As, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, Mn, Mo, Ni, Pb, Sb, Se, Si, Ti, Zn, and Zr.

Since weathering leads to oxidation of sulfide to form sulfate, sink-float separations, particularly for pyrites, are more efficient before the coal is ground and stored for a long time. The effluent from the sink-float operation and the runoff from the debris piles present problems, but they are preferable to those emissions created by combustion of the sulfates and pyrites. A very exhaustive review of the whole subject of coal preparation and the resulting wastes has been made by Wewerka et al. (136). They considered over 4400 references (through mid-1975) and have compiled a periodically updated computerized database which is available upon request at Los Alamos Scientific Laboratory. While their main concern was washing at the mine site, much of the data and many of the citations apply as well to preparation at the combustion site. The full report is an ERDA publication, and a useful summary may be found in Torrey (16).

In 1976, Mezey et al. (117) reviewed the technology, results and problems of coal washing and separation. They also included a 214 entry citation list on coal cleaning, and 82 references on contaminant removal from petroleum.

Preprocessing will improve the quality of coal. Not only is inorganic material partially removed, but the Btu-per-ton value is increased as the coal is upgraded by removal of noncombustibles. If fewer trace metals enter the boiler, certainly less are emitted. Besides those already mentioned, other articles which discuss preprocessing, its benefits and tradeoffs relating to trace metals, include: Ford (137), Manahan (138), Schultz et al. (139-140), Stambaugh et al. (141), Williams et al. (142, 143), Cavallaro et al. (144), Wewerka et al. (145), Wewerka et al. (146), and Capes et al. (147).

3.4 FLY ASH FORMATION MECHANISMS

In recent years, several studies have considered how fly ash particles form. Of principal concern is the effect of the form of the element in the fuel upon its ultimate fate. The experimental approach used in most of these inquiries was to measure elemental concentration as a function of fly ash particle size. The idea, following Natusch (148, 149), is that the smaller, spherical fly ash particles have a greater relative surface area than larger particles. Thus, elements which tend to be volatilized in combustion will condense in the off-gas stream on any available surfaces and thereby be enriched in the small particle fraction. Natusch predicts a simple inverse dependence (concentration, C, is inversely proportional to size, $C \alpha D^{-1}$, where D is diameter). Flagan and Friedlander (150), using a more complex theory involving a dependence upon the gas viscosity (the Knudsen number), predict a $C \alpha D^{-2}$ dependence in regions where the Knudsen number is less than 1 (the coninuum regime). Results vary from one study to another, but the Natusch model appears to be in better agreement with the data (151).

Although agreement is not universal, the consensus of several studies (36, 37, 40, 44, 45, 151-158) is that the more volatile elements show a preference for small fly ash particles (e.g., As, Zn, Sb, Se, Pb, Ga, Cd, Cr, Hg, Ni, Tl, V, Co). Various studies include other trace metals in their enrichment lists. The "volatility" of an element seems to be best correlated with the melting point of the oxide, although there are prominent exceptions. Most other metals show no enrichment versus particle size and some even decrease with decreasing particle size. Gladney et al. (40) show a decrease for Fe and Ce; they postulate the Fe concentration decrease is due to most of the Fe being introduced in a pyrite form which behaves differently from the organic phase during combustion; however, the same speculation will not account for the decrease in Ce. Smith, Campbell and Nielson (151, 153) point out that the fly ash matrix is composed mostly of Al, Mg and Si, and for very small particles a slight decrease in these elements is to be expected. That is, the increasing concentration of trace metals "dilutes" the matrix elements. Indeed, they observe a significant dilution of Si for smaller particle sizes, although not for Al, Fe or Mg. Ondov et al. (159) also report a decrease for silicon.

Campbell et al. (153) observed that fly ash is not homogenous, and that some particles are selective enriched only in certain elements. They have also observed more complex curves of concentration versus size, some with local maxima and minima indicating a more subtle behavior than predicted by the Natusch model. Almost all authors agree on the need for additional and more direct research on this problem. No model has been positively confirmed. And this subject is of great concern because the smaller particles, which do seem to have higher concentrations of certain trace elements, pass more readily through most types of control devices, are most mobile and long-lived in the atmosphere, are most active in the environment, and have the greatest residence time in the lungs (37). All of these effects are treated specifically elsewhere in this report.

Results pertaining to sink-float separation of ground coal have been discussed elsewhere, see Section 3.1.3. The primary consideration in that work was the separation of inorganic material. It has also been proposed (see references in that paragraph and 37, 151) that the location of the trace element in the coal plays a key role in its fate upon combustion. The idea is that trace elements bound in the organic phase are atomized during combustion, whereas those occluded with the mineral matter in the coal are less likely to be vaporized. If the "condensation on the fly ash surface" theory is valid, then those elements showing a high degree of organic affinity ought to show a more prominent inverse dependence of concentration with size. However, the correlation is not supported by the evidence. For example, of the 13 elements usually found to be enriched in the small particle fraction (see above), four are in Gluskoter's (29) list of high inorganic affinity (Hg, Cd, Pb, Zn) and four more are in the inorganic association category (Co, Ni, Cr, Se). Furthermore, none of his strong organic affinity elements made the list of commonly enriched elements (Ge, Be, B). Although the ideas seem plausible, they do not account for the behavior of the elements. Again, the metal oxide boiling point seems to provide the greatest degree of empirical correlation.

Zimmerman et al. (160) have studied the formation of metallic aerosols from different sources, one of which was combustion. They paid particular attention to mechanism of nucleation and particle size characteristics. Hulett et al. (49), as part of the continuing ORNL study at the Allen Steam Plant in Memphis, have looked at fly ash particles with a scanning electron microscope (SEM) and photoelectron spectroscopy. They found particle (matrix) composition to vary greatly as a function of size. Distinct composition differences were found when they compared the outside to the inside of fly ash particles. They reported sulfates concentrated on the particle surface, and that the surface of urban aerosols was higher in trace metals than aerosols collected in a steam plant.

Work on the trace metal concentration and particle size is continuing at Battelle's Pacific Northwest Laboratory in Richland, Washington; at Lawrence Livermore Laboratory in Livermore, California; and at the University of New Hampshire. At New Hampshire, Ulrich is carrying on a more direct approach in the study of fly ash formation. With Ulrich, French (161) has reported a combination of experimental and theoretical studies that show larger fly ash particles are formed from molten minerals in the boiler.

They further report that the low concentrations of metal oxides in boiler flue gas indicate that the more volatile oxides appear to participate directly in the condensation, nucleation and growth of sub-micron fly ash particles in the boiler. They conclude that, while the surface area phenomenon may be operative, one cannot neglect the possibility of different formation mechanisms for smaller particles which entrap larger concentrations of the trace metal oxides.

3.5 MISCELLANEOUS TOPICS

This section describes a series of unrelated articles on rather isolated topics that do not fit conveniently into any of the above categories. All of these articles are relevant to a study of trace metal emissions from SCCP's, but their emphasis is on fuel characteristics.

Bolding (1) emphasizes that the trace element concentrations of coal should be classified by amount of pollutant per Btu, the true measure of a fuel source. Furthermore, he analyzes the future increase in coal use and warns that the trend toward larger power plants may exacerbate the pollution problem beyond current predictions.

Joyce and Higer (162) at NASA have found that remote sensing of coal fields (via satellite) is able to classify fossil fuels by several qualities: organic and inorganic sulfur, ash content, coking qualities, detailed petrology and trace element content. Hence, a more accurate survey of the pollutant content of our coal reserves is possible. This remote sensing is also useful for establishing baseline data for many types of pollution, and would be useful in siting studies.

Metal-containing additives are used in many oil-fired SCCP's to improve boiler cleanliness, to reduce corrosion, to reduce stack emissions and plumes by improving flue gas and ash handling characteristics, and to help maintain design steam temperatures. These additives nearly always are oxides or hydrates of magnesium, manganese, or mixtures of the two with smaller amounts of aluminum. The use of these additives necessarily increase the potential emissions of these metals. Kukin (163) has reviewed the subject of such additives to oil-fired furnaces. Harker _et al_. (164)

at Lawrence Berkeley Laboratory have reported (although in a foreign journal) on the use of methyl cyclopentadienyl manganese tricarbonyl (MMT) in gas turbine combustors. They find that there is an optimum level to control particulate emissions, and that the manganese is intimately bound in the effluent particulate matter as manganese monoxide. They report a similar behavior for oil burning furnaces and power generation turbines.

Walker et al. (165) have written a report concerned with the catalysis of coal conversion to liquid or gaseous fuel. While this process does not fall under the definition of the SCCP constraint, they found it necessary to review the subject of minerals and trace elements in coal in order to understand catalytic behavior. Although much of the information they developed has also been reported elsewhere by Gluskoter, (28; see Section 3.1.3 of this report), a coauthor with Walker on this project, the work, references, and recommended research programs are worthy of note.

Zimmerman et al. (160) with the EPA have prepared a review report on metal aerosols. While much of the report is not germane to emissions from SCCP's, metal aerosol formation from combustion and metallic vapor condensation, both of which are relevant to fly ash formation processes, are reviewed.

3.6 RESEARCH NEEDS

By and large, the generalized characterization of coals is one of the areas where research has been sufficient. The only area deficient in data would be low temperature ashing and whole coals, yet these areas are fairly well represented in the literature. Of course, variations in individual coals preclude the use of generalized trace metal concentrations with any specific coal. Trace metals in petroleum show even wider individual variances, and for many purposes, each crude oil must be considered separately. The problem is even greater with residual oils, where trace metal analyses are seldom made. The team at Maryland has studied urban refuse and produced sufficient data to characterize the fuel; a corroberative study would be reassuring. Trace metals in wood have been little studied, but conventionally, the organic pollutants have attracted far more attention.

Although the form of the trace elements in coal have been studied, see Section 3.1.3, the importance of the inorganically versus organically bound trace metals on their fate during and after combustion remains uncertain. Various theories have been proposed and certain studies seem to report data relating trace metal concentrations to various parameters, but the data vary from one experiment to another and no theory is supported unanimously. The theory of Natusch, which presumes that the volatile metals condense on the fly ash surfaces, seems to be most popular; however, some of the evidence does not support it. Thus, a greater understanding of the fly ash formation processes, particularly due to the influence of the trace metal forms in the coal, is needed. This may be accomplished, in part, by a more detailed study of the location of the trace metals on or in the fly ash particles.

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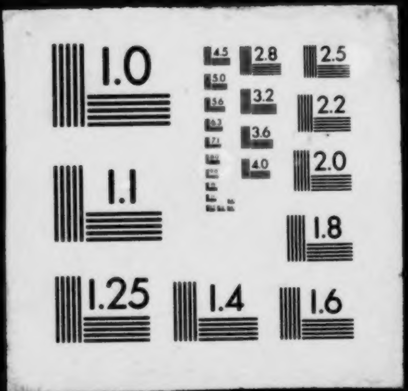
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SECTION 4

CONTROL TECHNOLOGY

A typical coal-fired power plant includes a combustion unit and various support or subsystems. Fine particles and/or trace elements are emitted from the combustion unit as well as from some of the subsystems (1,2). This analysis is primarily focused on the emission of pollutants from the combustion process to the atmosphere; a discussion of the emissions from utility subsystems is included for completeness. The sources of major power plant wastestreams (listed in Table 4-1 and shown schematically in Figure 4-1) are discussed in the following sections. The techniques used by the utility industry to control or treat the wastestreams are also described.

4.1 TRACE ELEMENTS FROM SUBSYSTEMS

The utility subsystems which may emit trace elements include: (1) coal storage and preparation, (2) raw water treatment, (3) metal cleaning, (4) cooling water system, (5) floor and yard drainage, and (6) ash handling and disposal. Each of these topics is discussed below.

4.1.1 Coal Storage and Preparation

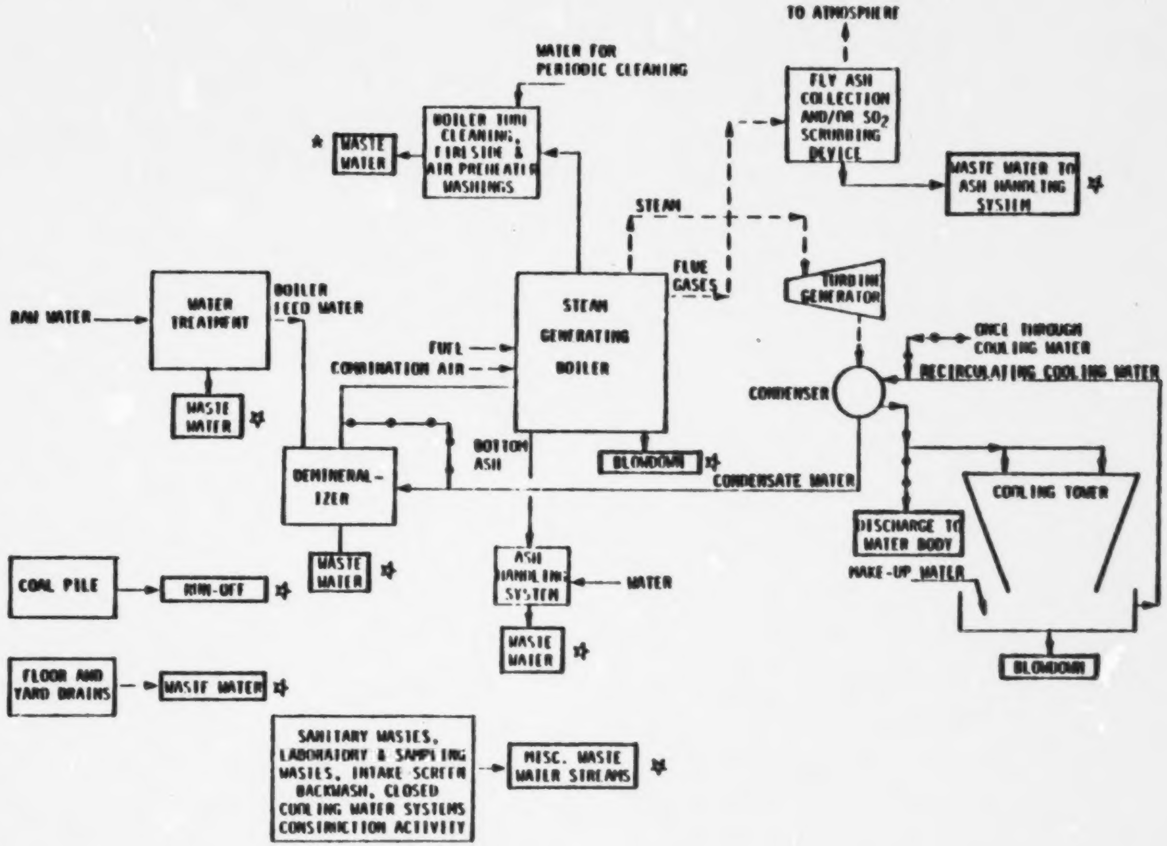
Before coal is utilized in a combustion process, it is normally sized and as much ash (inert materials) and pyritic sulfur as possible are removed (3). Although a large portion of this coal preparation procedure is conducted at the mining site, the coal may undergo further preparation at the plant site before being stored in piles.

4.1.1.1 Waste Characterization and Control --

Environmentally unacceptable wastestreams are generated by various phases of the coal storage and preparation system. Fine dust is generated

TABLE 4-1. VARIOUS UTILITY PLANT WASTESTREAMS AND THEIR SOURCE

	Waste Streams		
Source	Aqueous	Gaseous	Solid
Coal storage and preparation	Coal pile runoff, Drainage		Particulate Matter
Raw water treating	Sludge		
Combustion process	Boiler Blow Down	Flue gas and fly ash aerosols	Bottom ash
Ash handling	Sluiced Ash		Dry Ash
Metal cleaning	Cleaning wastestream		
Cooling system	Cooling tower Blow Down		
Floor and Yard Drain	Wastewater		
Air pollution control	SO_2 sludge, sluiced particles		


TO ATMOSPHERE
WATER FOR PERIODIC CLEANING
FLY ASH COLLECTION AND/OR SO2 SCRUBBING DEVICE
WASTE WATER
BOILER TUBE CLEANING, FIRESIDE & AIR PREHEATER WASHINGS
WASTE WATER TO ASH HANDLING SYSTEM
STEAM
FLUE GASES
RAW WATER
WATER TREATMENT
BOILER FEED WATER
STEAM GENERATING BOILER
FUEL
COMBINATION AIR
TURBINE GENERATOR
ONCE THROUGH COOLING WATER
RECIRCULATING COOLING WATER
CONDENSER
WASTE WATER
BOTTOM ASH
BLOWDOWN
CONDENSATE WATER
DEMINERALIZER
COOLING TOWER
DISCHARGE TO WATER BODY
MAKE-UP WATER
COAL PILE
RUN-OFF
WASTE WATER
ASH HANDLING SYSTEM
WATER
WASTE WATER
BLOWDOWN
FLOOR AND YARD DRAINS
WASTE WATER
SANITARY WASTES, LABORATORY & SAMPLING WASTES, INTAKE SCREEN BACKWASH, CLOSED COOLING WATER SYSTEMS CONSTRUCTION ACTIVITY
MISC. WASTE WATER STREAMS

* Wastewater that may be reused in plant or must be treated before being discharged to environment.

Figure 4-1. Simplified schematic of a typical power plant.

Source: (4)

during the coal sizing operation, but these emissions can be adequately controlled with the use of water sprays. This, however, converts an air pollution problem into a water pollution problem. The resulting wastewater is combined with the runoff from the coal storage piles.

In many sections of the country, the runoff from coal processing wastes or mining activities has become a serious problem (1). Because of the similarities between these wastes and coal storage in piles at the plant site, it is anticipated that runoff from these piles could also be a serious problem. The actual volume of coal pile runoff as well as its composition is affected by the composition of the coal, surface area of the pile, and amount of rainfall (2). In general, the coal reacts with rain and oxygen to convert metal sulfides to sulfuric acid (2, 4-6). The acid can, in turn, dissolve many other complex metallic sulfides, sulfates, and sulfites, releasing some or all the following trace metals: aluminum, zinc, copper, cadmium, beryllium, nickel, chromium, vanadium, silver, and lead. Major chemical constituents of coal pile runoff and their composite range of concentrations are presented in Table 4-2 (2). Because of the various contaminants in and the volume of runoff (approximately 17-26 million gallons per year based on 43-60 inch of rain per year), coal pile runoff represents a serious threat to waterways or aquifers (4). In some plants, impervious liners are normally used in these ponds as well as underneath the coal piles in order to prevent seepage that could contaminate groundwater aquifers (4). Coal pile runoff, which typically has a pH of 2-6 and high dissolved solids content, is normally routed to an evaporation pond. Runoff having a pH of 6-5 and low dissolved solids content can be routed, along with other wastestreams, to an ash pond depending on available pond area (4).

4.1.1.2 Gaseous Emissions--

Under certain conditions, the oxidation of the coal or other mineral matter can produce sufficient heat to ignite the interior of the pile. As a result, coal piles may also be the source of noxious odors and vaporous trace metal emissions whenever the coal piles spontaneously ignite. One study has shown that trace element emissions from burning coal piles are

TABLE 4-2. CONSTITUENTS OF COAL PILE RUNOFF

	Range
Conventional Measures of Pollution	
pH	2.1 - 6.6
	(mg/l)
Total Suspended Solids	22.000 - 610.000
Total Dissolved Solids	720.000 - 28,970.000
Turbidity	2.770 - 505.000
Total Hardness	130.000 - 1.851.000
Major Chemical Constituents	
Ammonia	0.000 - 1.770
Nitrate	0.300 - 1.900
Phosphorus	0.200 - 1.200
Sulfate	130.000 - 20,000.000
Chloride	3.600 - 481.000
Aluminum	66.000 - 1,200.000
Iron	0.060 - 4,700.000
Manganese	90.000 - 180.000
Sodium	160.000 - 1,260.000
Trace Element Constituents	
Arsenic	0.005 - 0.600
Beryllium	<0.010 - 0.070
Cadmium	<0.001 - 0.003
Chromium	0.000 - 16.000
Cobalt	0.025 - - -
Copper	0.010 - 3.900
Magnesium	0.000 - 174.000
Mercury	<0.0002- 0.007
Nickel	0.240 - 0.750
Selenium	<0.001 - 0.030
Zinc	0.006 - 12.500

Source: (2)

a potentially serious environmental problem, particularly at the local level, and concluded that this possibility needs to be comprehensively assessed (5).

4.1.2 Raw Water Treatment

Good quality water is required for the generation of steam in a utility plant. The quality of boiler feed water can vary as is required by the boiler's operating pressure (4). Today's high pressure, high-temperature boilers require a controlled stream of high quality water which can be achieved by various treatment processes. Among these processes are clarification, lime-soda softening, ion exchange, and filtration (2.4). Operation of the softening, clarification, and filtration processes results in the generation of a "sludge" which consists of 0.5-5.0 percent suspended solids and contains chemical additives such as phosphate, caustic soda, lime, and alum. Treatment of these sludges typically involves hydraulic thickening to a content of 15-20 percent solids. After thickening, the sludges are dewatered and the solids disposed of in a landfill (2, 4).

When an ion exchange process is used, a wastestream containing waste regenerants (sulfuric acid and sodium hydroxide) and rinse water is generated. This stream is normally collected in a neutralization tank and its pH adjusted to the range of 6.0-9.0. Any precipitates formed upon neutralization are separated from the liquid by settling or filtration and then disposed of in a landfill. The overflow can be reused or discharged to the environment (4).

4.1.3 Metal Cleaning

Because the efficiency of a power plant is dependent on the cleanliness of the various heat transfer surfaces in the plant, these surfaces are cleaned regularly. Equipment that must be cleaned includes the boiler, boiler fireside, air preheater, stack cooling tower basin, as well as miscellaneous small equipment. Strong chemicals are normally utilized in the cleaning process and ideally, the surfaces are cleaned to the "bare metal." Consequently, some of the metal is dissolved in the cleaning solution. Iron, copper, nickel, zinc, and chromium are the metals commonly found in the wastestream from this treatment process (2) .

Many utilities discharge their cleaning wastes with once-through cooling water, relying on the resulting high dilution ratio to minimize the adverse effects of discharge. Other utilities collect this wastestream in storage basins or ash ponds and adjust the pH to the neutral range. The less soluble compounds precipitate from the water, and "clean" water is discharged from the plant. The settled solids are periodically cleaned from the pond and disposed of in landfills (4, 7).

4.1.4 Cooling Water System

The cooling water used in a power plant must be free of biological growth in order to prevent fouling of the heat transfer surfaces. Various chemicals can be used to control biological growth in the cooling water. For instance, chlorine and/or organic chemicals are normally used for biological control in a once-through cooling system (2, 4). Consequently, the discharge from such a system would contain these components. Since once-through cooling water may contain some dissolved trace metals such as copper, they could also be expected to be present in the effluent. The level of residual chlorine in the effluent can be controlled by employing an intermittent program of chlorine or hypochlorite addition. Another technique that can be used to reduce the level of residual chlorine discharged is to employ chlorination at periods of low condenser flow (2, 4).

In a closed, recirculating, cooling system a blowdown is required to prevent scaling of the condenser. The blowdown stream contains dissolved solids, residual chlorine, and chromates (4, 7). Reducing the level of residual chlorine being discharged can be achieved by the same techniques employed in a once-through system. An end-of-pipe treatment for reducing chlorine levels is the addition of a reducing agent such as sodium bisulfite; however, an excess of this chemical creates an oxygen demand, thus trading one potential water problem for another (4).

4.1.5 Floor and Yard Drainage

Floor and yard drainage from a coal-fired power plant generally contains dust, fly ash, coal dust, and floor scrubbing detergent (4). This wastestream may also contain lubricating oil or other oils resulting from pump seal leakage or oil spills. This wastestream can be combined with coal pile runoff and treated accordingly (7).

4.1.6 Ash Handling and Disposal

Bottom ash generated by the combustion process is rejected by this process and sent to final disposal via the ash handling system. Disposal of the ash is achieved by a water sluicing system to an ash pond or by a pneumatic conveying system to a landfill site (2). In both of these disposal methods, the possibility of trace metals leaching from the ash and contaminating local groundwaters should be considered (8). Several alternatives to these disposal techniques have been found and include use of ash as a:

- source for recovering various metals,
- skid-retardant aggregate in highways, and
- replacement for a portion of the cement in concrete mix (9-15).

Efforts for the utilization of ash in the areas of sanitary landfills, agriculture and land reclamation, and coal mine fire control are being explored (12, 16).

4.2 FINE PARTICLES AND TRACE ELEMENTS FROM THE COMBUSTION PROCESS

4.2.1 Boiler Blowdown Characterization

The coal combustion process is the source of three wastestreams: boiler blowdown, bottom ash, and flue gases with suspended particles. Boiler blowdown is the result of an attempt to control the scaling of dissolved solids in the boiler feed water on to the boiler surfaces. Boiler blowdown is principally a source of soluble salts, but it commonly contains iron and copper (2, 7). Normally, this stream is of high enough quality to be reused in various portions of the plant. The most desirable reuse of boiler blowdown is as makeup to the demineralizer system (7).

4.2.2 Bottom Ash Characterization

Coal-fired combustion processes generate two types of ash, fly ash and bottom ash. Fly ash exits the boiler with the flue gas and will be discussed later; bottom ash exits at the bottom of the boiler. Bottom ash varies in quantity and composition depending on the type of fuel utilized, method of combustion, and point in the boiler from which it is obtained (2). Typically, the bottom ash contains various metals such as arsenic, cadmium, cesium, cobalt, chromium, copper, mercury, magnesium, manganese, sodium, nickel, lead, tin, selenium, titantium, iron, aluminum, gallium, germanium, vanadium, and uranium (2, 9, 11, 17, 18). The bottom ash is disposed of via the ash handling system as described above.

4.2.3 Flue Gas Characterization

The flue gas from all fossil-fuel combustion processes (except those fired with natural gas) contain SO_2, NO_x, particles, and various trace elements that are present in the fuel. Particulate emissions from combustion processes can vary depending on the composition of the fuel, type of combustion process used, quantity of excess air used for combustion, as well as other operating practices (19). Typical loadings and particle size distributions for fly ash discharged from various types of coal-fired boilers are presented in Table 4-3. The data in this table show that pulverized coal boilers produce the heaviest dust loadings. The finest particulate emissions are generated by cyclone boilers (3). The results of a test in which the emissions generated by an oil-fired and coal-fired industrial boiler were compared showed that the quantity of particles from oil firing is considerably less than from coal firing (20). However, the particles from oil firing are generally smaller and more difficult to remove from the flue gas (20).

Although the data in Table 4-3 do not characterize the distribution of particles that are less than 10 microns (μm) in diameter, these particles (particularly, those less than 5 μm) have been reported to significantly contribute to all major adverse aspects of air pollution (21). For instance, visibility reduction associated with air pollution is primarily a result of 0.1-1.0 μm diameter particles in the atmosphere (21, 22). Several researchers have also shown that the greatest pulmonary deposition is exhibited by the smallest particles emitted from a combustion or incineration process (23-28). More complete distribution data for particles from various boilers

TABLE 4-3. TYPICAL AMOUNT AND SIZE OF FLY ASH EMISSIONS FROM VARIOUS BOILERS

				Pulverized Coal		
		Underfeed Stoker	Spreader Stoker	Dry[1] Bottom	Slag[2] Tap	Cyclone Furnace
Carry-over, fraction of ash in coal, %[3]		20-30	30-80	60-85	45-55	10-15
Combustible content, %		10-50	20-60	5-10	5-10	5
Dust loading, lb/1000 lb gas[4]		0.5-4	1.5-10	6-9	4-6	0.6-1.5
Typical size consist, cumulative percent						
Microns	Mesh					
< 10		7	11	40		86
< 20		15	23	70		91
< 44	325	30	42	80		95
< 74	200	38	56	97		98
<149	100	57	73	100		100

[1] Ash exits furnace as a dry solid
[2] Ash exits furnace as molten liquid
[3] Includes combustibles
[4] Based on coal having 15% ash content dust in gas leaving furnace before any collectors. Corrected to 50% excess air.

Source: (3)

are presented in Figures 4-2, 4-3, and 4-4. The data presented in Figure 4-2 reflect data obtained from nine stoker-fired boilers, while Figures 4-3 and 4-4 summarize data from 300 pulverized coal and seven cyclone boilers, respectively (4). Particle size distribution data for emissions from industrial coal-fired boilers and municipal incinerators are presented in Figures 4-5 and 4-6. Comparison of these data shows that, while the details of each distribution are unique, the bulk of particles from all boiler types fall into similar size ranges for all types of sources. If the flue gas subsequently pass through an ESP, which removes particles above 2 µm quite efficiently, the final emissions compare even more closely.

Upon combustion, the trace metals in the coal are partitioned among the fly ash, bottom ash, and flue gas exiting the boiler. The presence of the various trace metals in the boiler effluents is dependent on their respective volatilities (29). A trace metal mass balance and partitioning study in which 37 trace elements were considered was conducted at the Allen Steam Plant (30). During this study the various trace elements were categorized into three groups according to their partitioning behavior; these groups are presented in Table 4-4. Although the data in Table 4-4 are the results observed in one plant, similar partitioning behaviors have been reported by other sources (23, 30-33). The partitioning of 27 trace elements between bottom and fly ash was also quantified for three power plants as shown in Table 4-5 (33).

These elements that vaporize at operating temperatures in the boiler (approximately 1500°C) may condense on the fly ash in the flue gas as the flue gas cools (5, 23, 29, 32, 34). These "condensable" trace elements (Class I and II elements in Table 4-4) are believed to condense on any available surface (17, 23, 29). Since the largest surface areas per unit of mass are exhibited by those particles having the smallest diameters (see Figure 4-7), the greatest trace element concentrations (mass basis) have been found on the smallest fly ash particles (23, 29, 30, 32, 35). There has been some speculation that trace element deposition on small particles is the result of adsorption of the trace element; however, Linton, et al. have reported that 80 percent of the trace elemental mass in particles

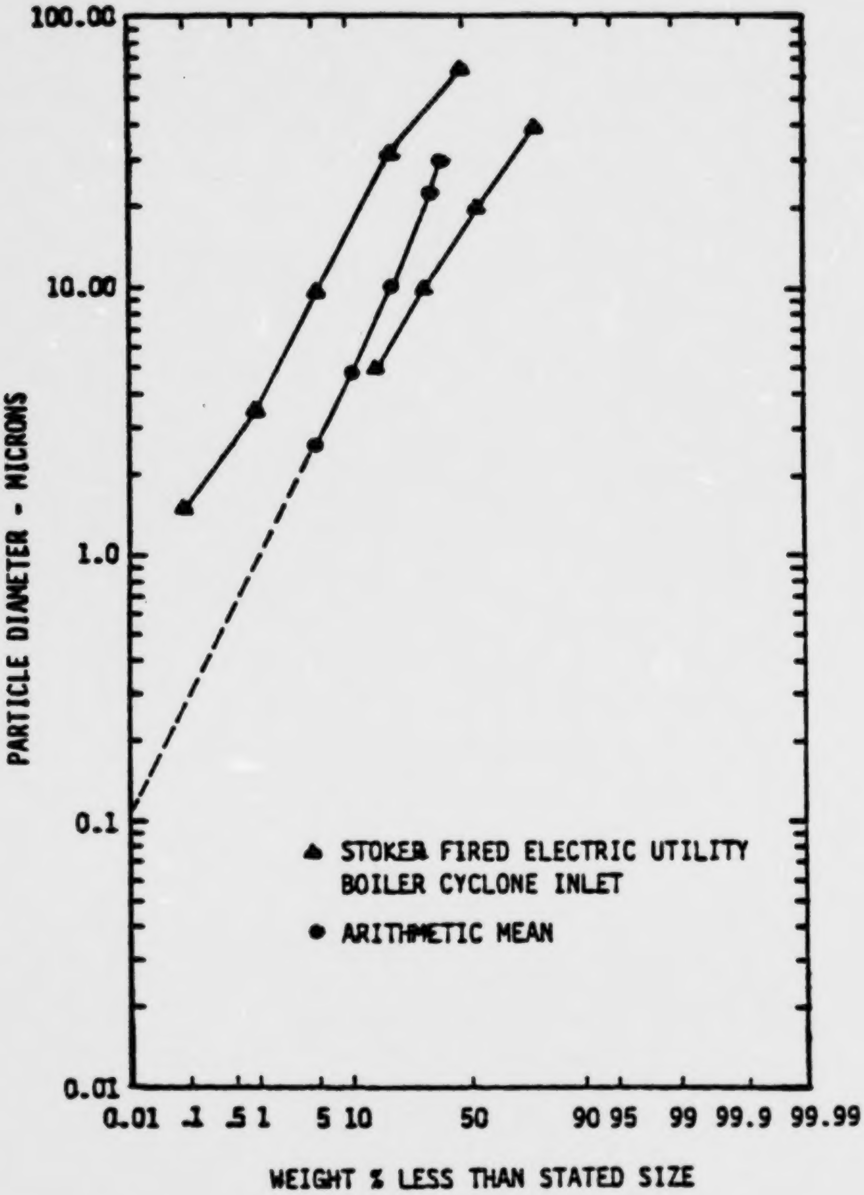


Figure 4-2. Particle-size distribution of particles emitted from uncontrolled power plants utilizing stoker coal-fired boilers.

Source: (17)

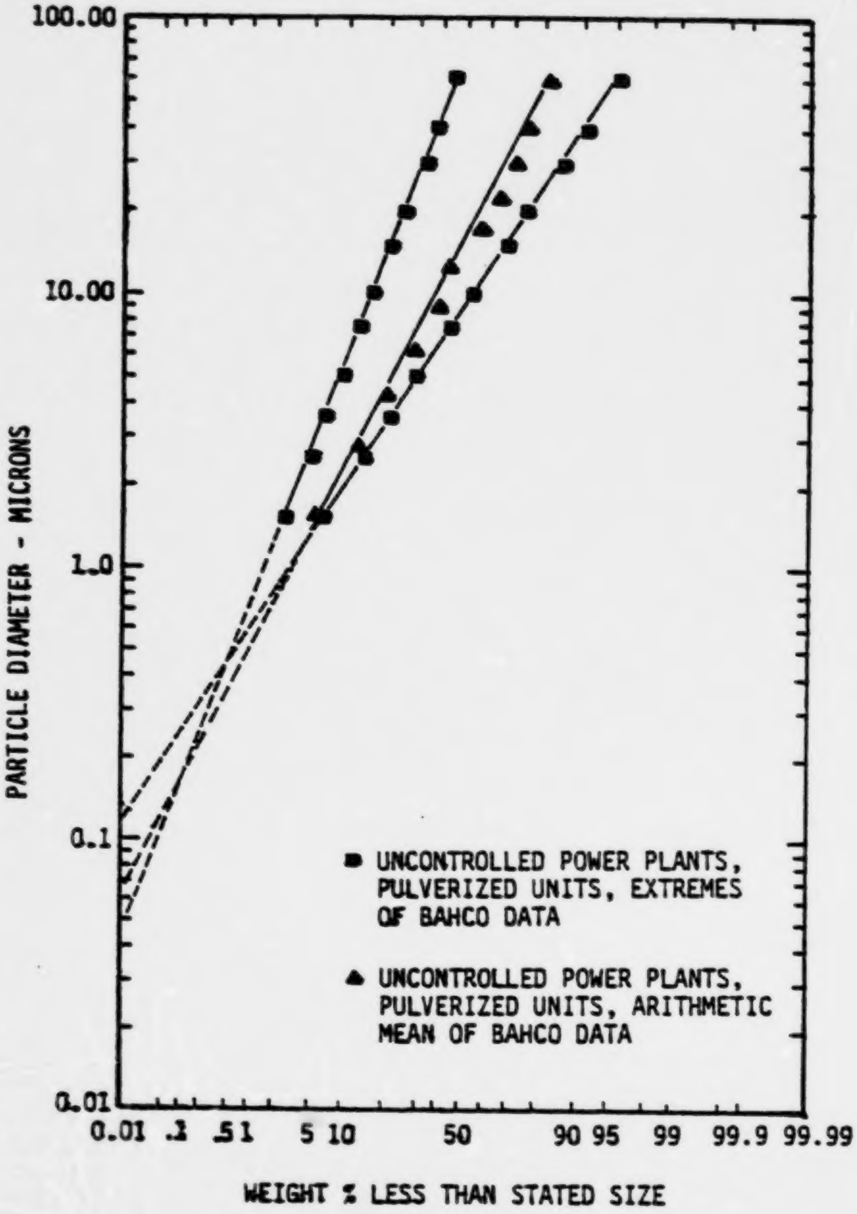


Figure 4-3. Particle-size distribution of particles emitted from uncontrolled power plants utilizing pulverized coal-fired boilers.

Source: (17)

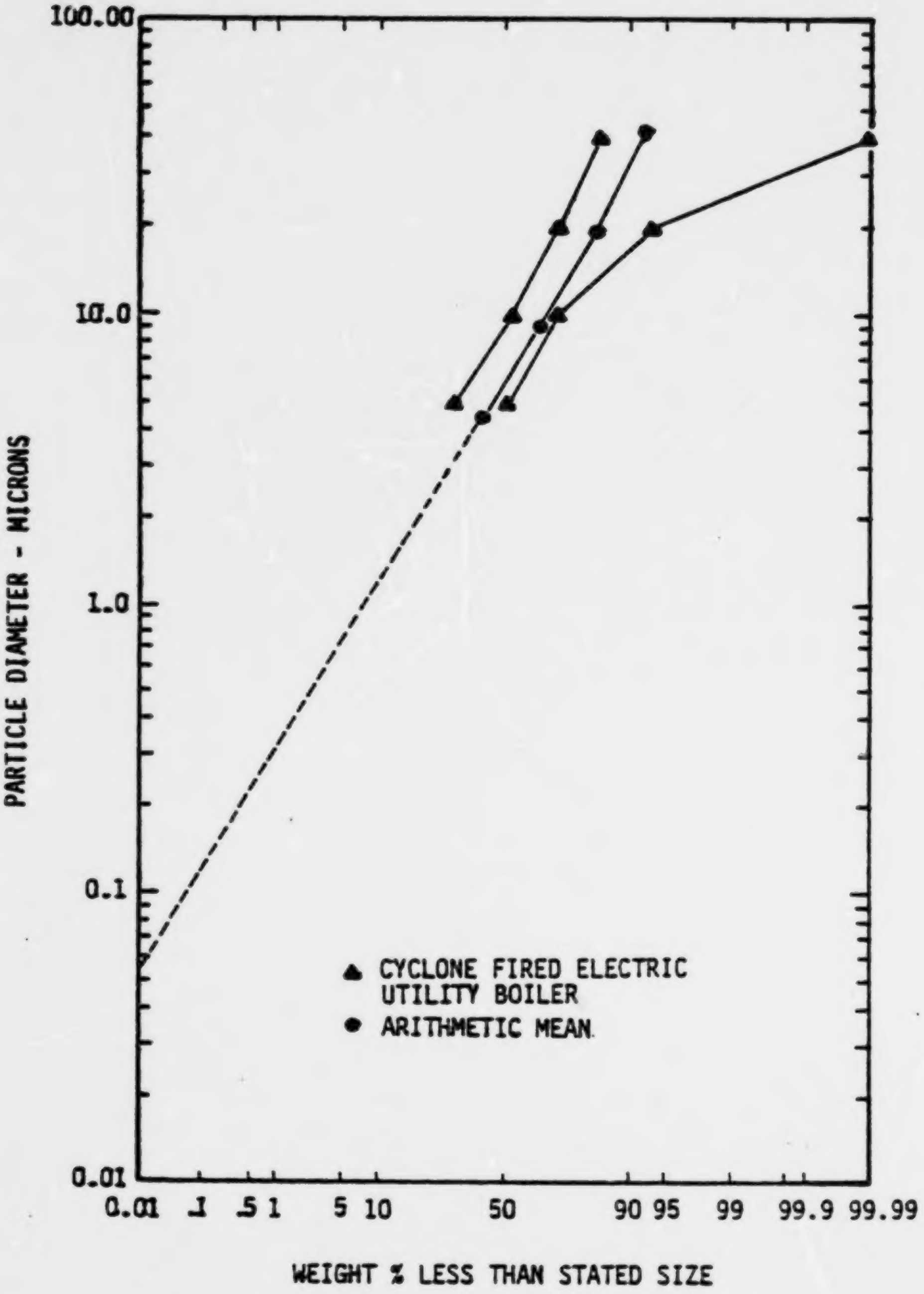


Figure 4-4. Particle-size distribution of particles emitted from uncontrolled power plants utilizing cyclone coal-fired boilers.

Source: (17)

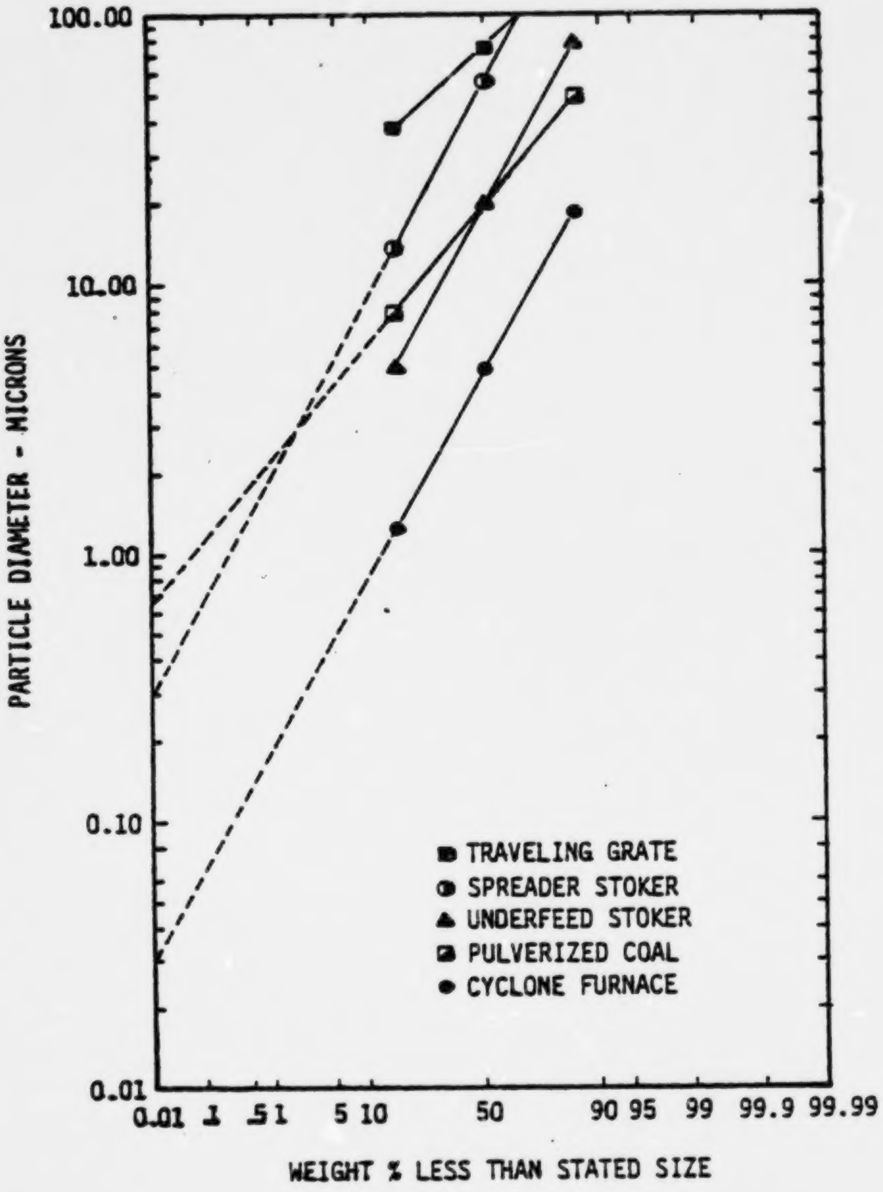


Figure 4-5. Particle-size distribution of particles emitted from uncontrolled industrial power plants (coal-fired)

Source: (17)

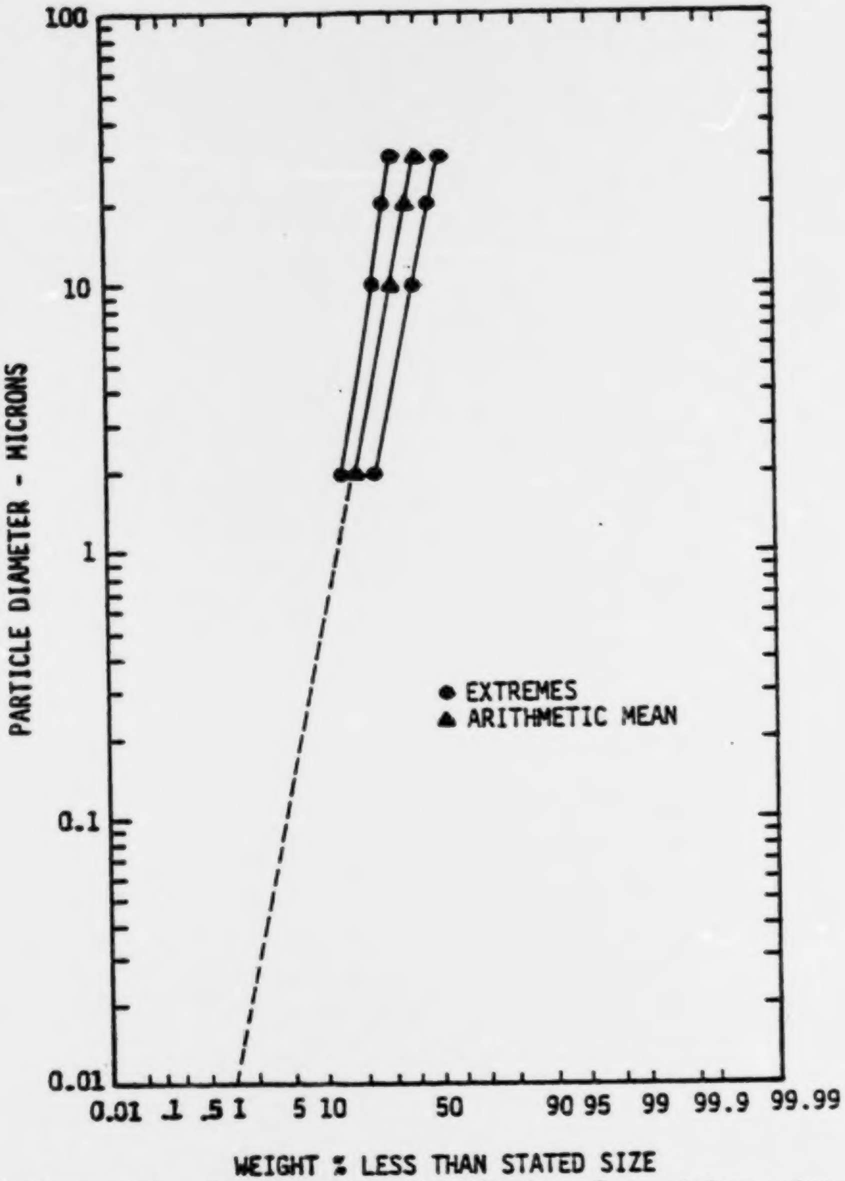


Figure 4-6. Particle-size distribution of particles emitted from uncontrolled municipal incinerators (Bahco data).

Source: (17)

TABLE 4-4. PARTITIONING BEHAVIOR OF TRACE ELEMENTS AT ALLEN STEAM PLANT

Group	Partitioning Behavior	Trace Element Symbol
Class I	Elements partition about equally between slag and fly ash exiting boiler	Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th, Ti
Class II	Elements are concentrated in boiler fly ash compared with the slag	As, Cd, Cu, Ga, Pb, Sb, Se, Zn
Class III	Elements remain essentially in the gas phase	Hg, Ce, Br

Note: (1) Elements, Cr, Cs, Na, Ni, U, and V appear to be between Classes I and II

(2) Cyclonic boilers used at Allen Steam Plant

Source: (30)

TABLE 4-5. ASH AND TRACE ELEMENT PARTITIONING OBSERVED IN THREE WESTERN POWER PLANTS UTILIZING PULVERIZED COAL AND CYCLONE BOILERS

	Pulverized Coal Boilers				Cyclone Boiler	
	Plant A[1]		Plant B[2]		Plant C[3]	
Component	Bottom Ash (% of Total)	Boiler Fly Ash (% of Total)	Bottom Ash (% of Total)	Boiler Fly Ash (% of Total)	Bottom Ash (% of Total)	Boiler Fly Ash (% of Total)
Ash	22.2	77.8	21.3	78.7	73.7	36.3
Aluminum	20.5	78.5	18.0	82.0	67.2	32.8
Antimony	2.7	97.3	9.9	90.0	15.9	84.1
Arsenic	0.8	99.0	5.0	95.1	16.9	83.1
Barium	16.0	83.9	15.4	84.4	64.9	34.9
Beryllium	16.9	82.0	15.7	84.4	58.5	41.5
Boron	12.1	87.9	7.9	92.1	21.0	78.9
Cadmium	15.7	84.3	8.9	91.1	26.8	73.5
Calcium	18.5	81.5	15.1	84.9	60.3	39.7
Chlorine	16.0	84.0	8.3	91.7	12.2	87.6
Chromium	13.9	86.1	10.7	89.3	44.2	55.7
Cobalt	15.6	84.4	15.5	84.4	48.0	53.9
Copper	12.7	87.3	12.4	87.6	34.1	66.1
Fluorine	1.1	98.9	0.0	100.0	1.1	98.9
Iron	27.9	72.1	20.4	80.6	61.8	38.2
Lead	10.3	89.7	3.1	96.8	7.8	92.3
Magnesium	17.2	82.8	17.7	82.3	62.1	37.9
Manganese	17.3	82.7	13.6	86.3	62.5	37.7
Mercury	2.1	97.9	0.8	99.3	0.8	99.2
Molybdenum	12.8	87.2	8.4	91.6	16.3	83.9
Nickel	13.6	86.4	18.3	81.6	22.7	77.1
Selenium	1.4	98.6	0.0	100.0	2.3	97.8
Silver	3.2	96.8	9.5	91.7	22.0	78.1
Sulfur	3.4	96.5	0.0	100.0	0.1	99.9
Titanium	21.1	78.9	20.6	79.3	69.2	30.9
Uranium	18.0	82.0	50.1	49.8	29.8	70.0
Vanadium	15.3	84.9	16.3	83.6	60.9	39.1
Zinc	29.4	70.6	4.4	95.5	13.3	86.9

[1] Plant A is a 350 MW unit with a tangentially-fired, pulverized coal boiler.
[2] Plant B is a 330 MW unit with a tangentially-fired, pulverized coal boiler.
[3] Plant C is a 250 MW unit with a cyclonic boiler, in which lignite is burned.

Source: (33)

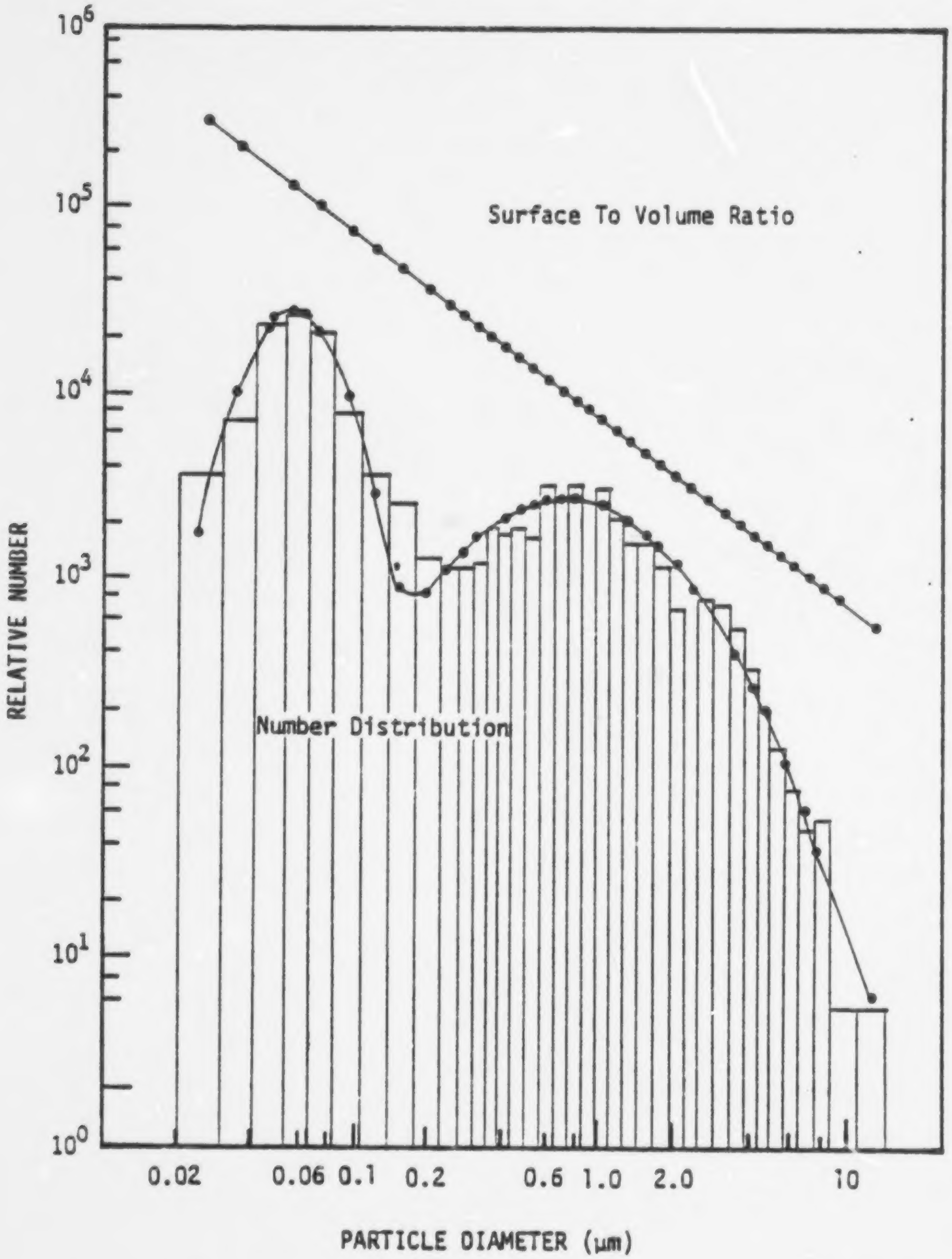


Figure 4-7. Plot of surface area to volume ratio as a function of particle size. The lower curve is typical of number distributions (of particles) found in fly ash.

Source: (35)

of 1 μm is present on the surface of the particle (32, 36). Several investigators have studied the variation in the concentrations of trace elements with respect to particle size (23, 29, 30, 35-37). Some of their observations are presented in Figures 4-8 through 4-12. The various processes that are normally used to control particulate emission from combustion processes and their effectiveness in controlling trace element emissions are discussed in the next section.

4.3 AIR POLLUTION CONTROL SYSTEMS

Until recently, the air pollutants with which the utility industry has been most concerned were particles, SO_2 and NO_x. Consequently, the primary purpose of the air pollution control system in the utility industry has been the reduction of gaseous (SO_2, NO_x) and particulate emissions. Since little concern has been given specifically to trace element emissions, no direct effort has been made to control these emissions (5, 21, 38-46); however, some reduction in trace element emissions is achieved by particle control processes due to the presence of trace elements on the fly ash (43, 47). The reduction that could be expected is difficult to quantify because the higher trace element concentrations are present on the smallest particles and control processes become less effective as the particles decrease in size (17, 36, 38, 40, 43, 48).

The four basic technologies that have been used in the utility industry to reduce gaseous and particulate emissions include: dry mechanical separators, electrostatic precipitators, wet scrubbers, and baghouses. These technologies are briefly described and their impact on trace element emissions are discussed below.

4.3.1 Dry Mechanical Separators

4.3.1.1 Process Description --

Cyclone (centrifugal) separators are one of several dry, mechanical collection devices that have been developed for particulate control. In most cases, the flue gas enters the separator tangentially at the top of the cylinderical section and spirals downward into a conically-shaped bottom; see Figure 4-13 (48). The particles, which have a greater applied centrifu-

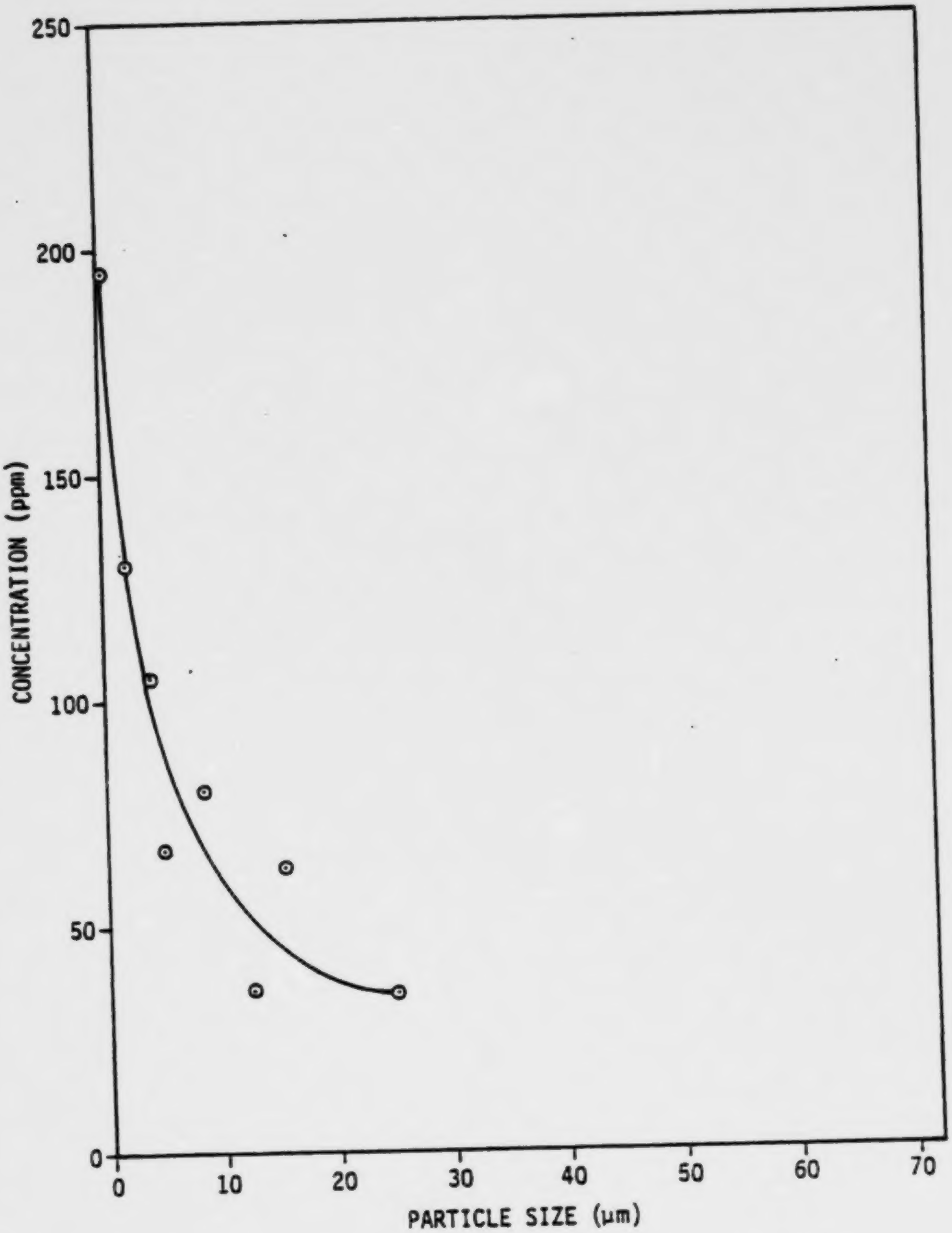


Figure 4-8. Concentration of nickel vs particle size.

Source: (37)

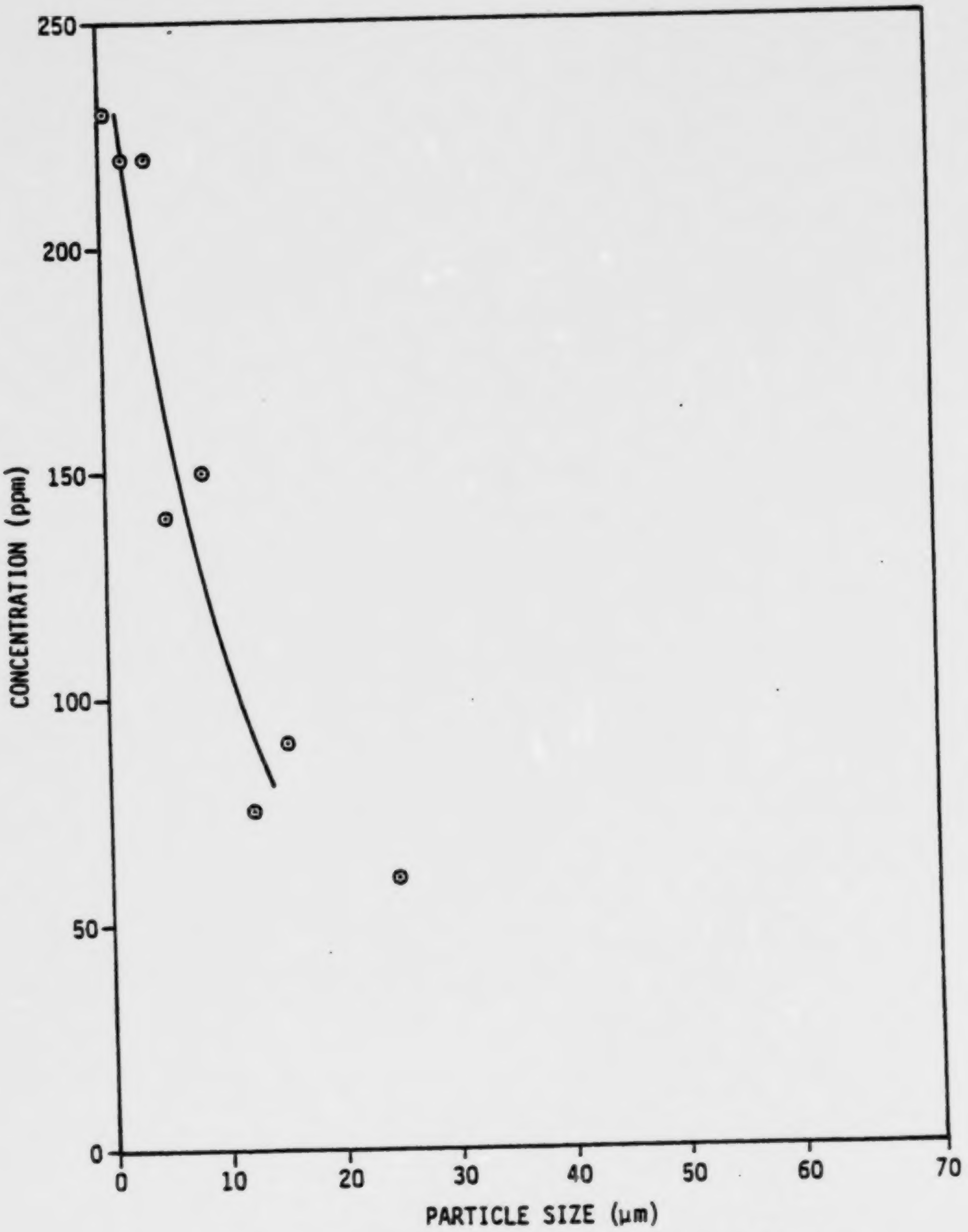


Figure 4-9. Concentration of chromium vs particle size.

Source: (37)

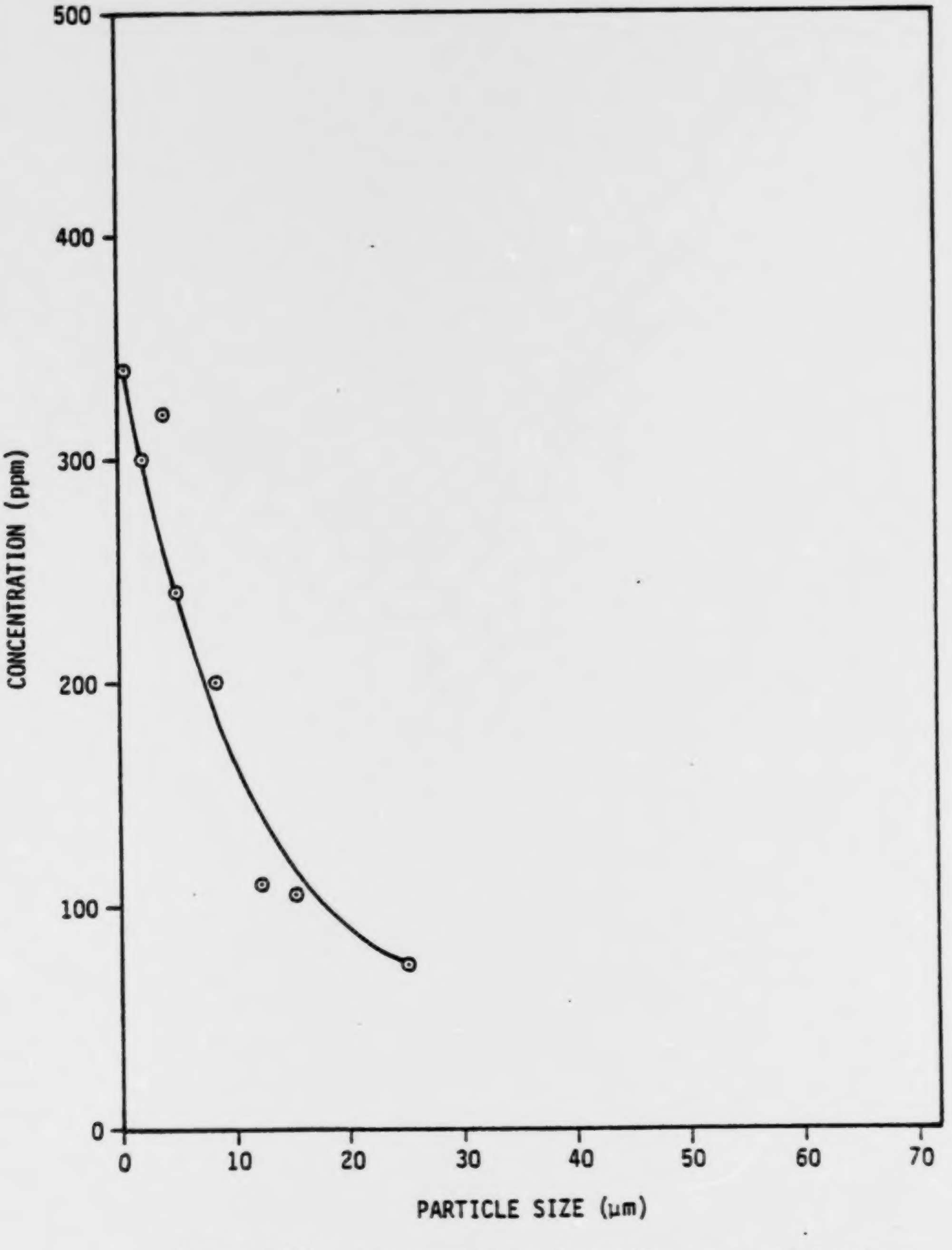


Figure 4-10. Concentration of vanadium *vs* particle size.

Source: (37)

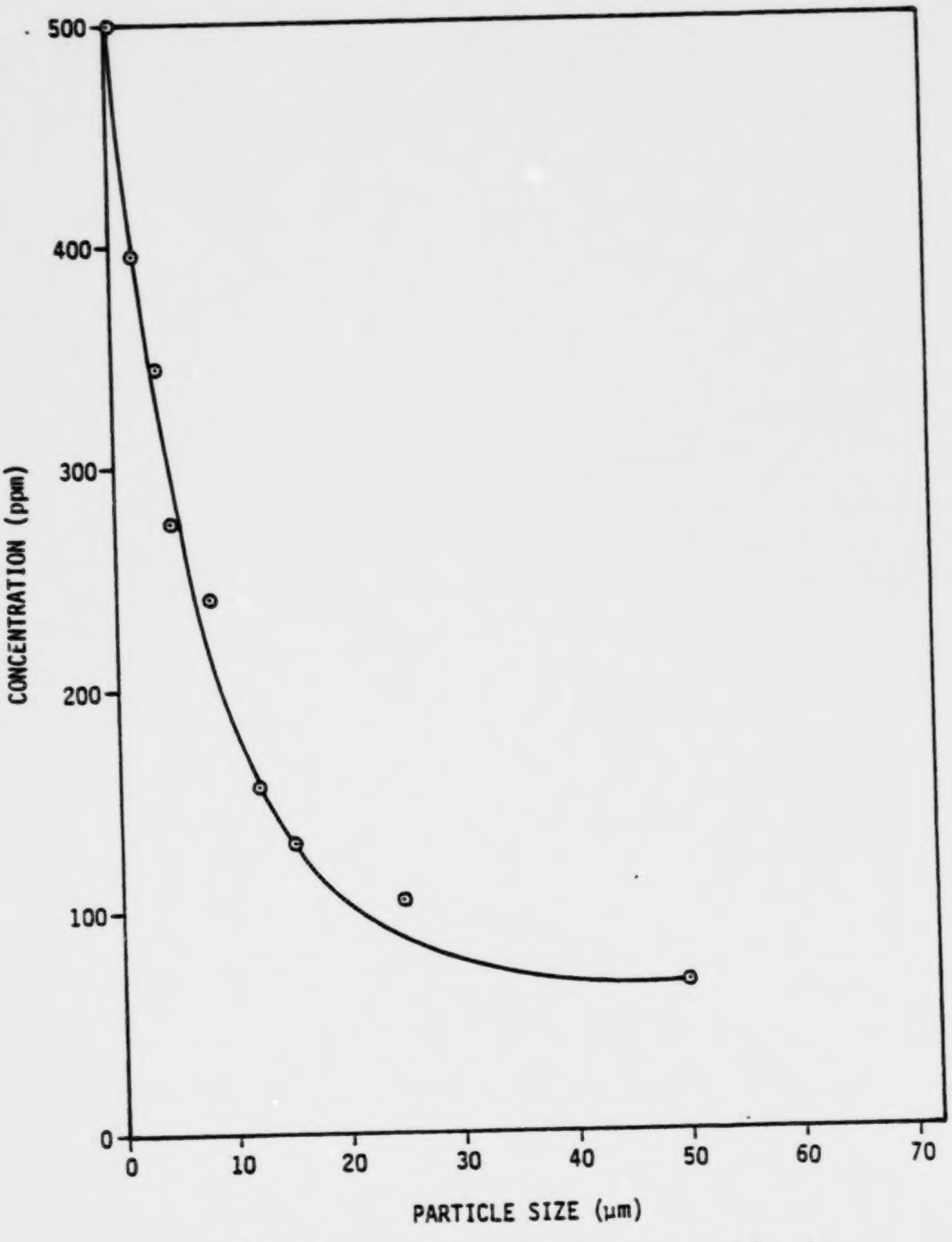


Figure 4-11. Concentration of copper vs particle size.

Source: (37)

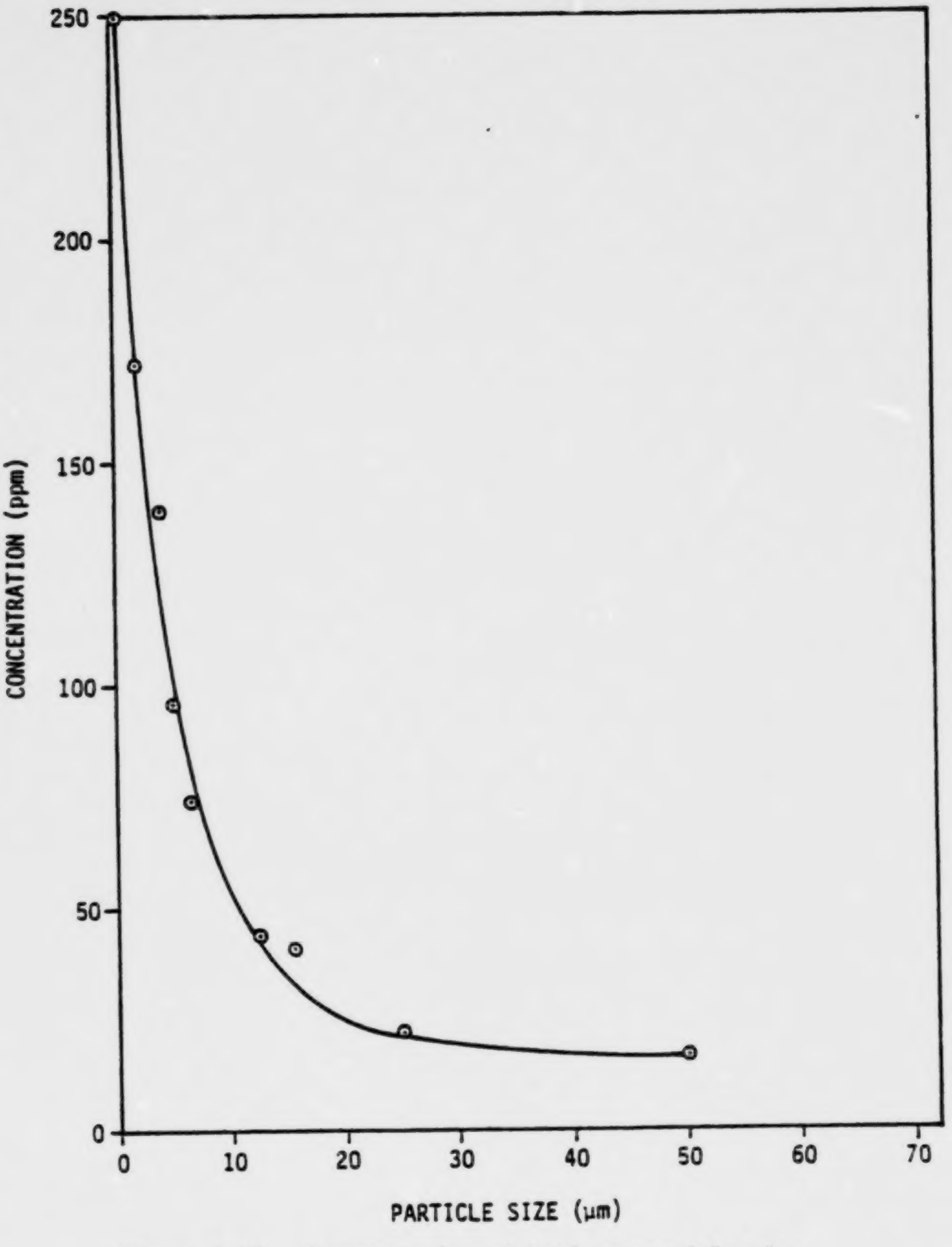


Figure 4-12. Concentration of lead *vs* particle size.

Source: (37)

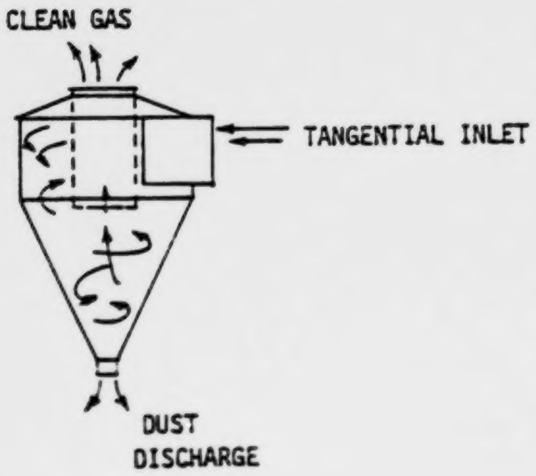

CLEAN GAS
TANGENTIAL INLET
DUST
DISCHARGE

Figure 4-13. Schematic of simple dry cyclone separator.
Source: (48)

gal force than the flue gas, accumulate at the wall and are carried down, against the wall, by the gas. The dust is discharged through the bottom while the flue gas flows back up in a small spiral vortex and exits at the top.

Cyclones can efficiently remove particulates of approximately 5 μm at dust loadings of 1-100 grains/ft^3 with only a moderate pressure drop (42, 48). Because of their ability to handle high dust loadings, cyclones seem to be best suited as a precleaning device for other processes. These separators are, generally, low in cost, have no moving parts, and can be constructed of materials that can withstand temperatures as high as 980°C (42, 48). The major disadvantage of cyclone separators is their relative inability to collect fine particles ($\leq$2 μm) without incurring substantial pressure drops (42, 48-50). Because of this disadvantage the utility industry is moving away from using cyclones; a survey conducted by Schwieger showed that 43 percent of recent or proposed boiler installations are not using or planning to use cyclones (51).

4.3.1.2 Impact on Trace Element Emissions --

Because data showing the trace element collection efficiency of a cyclone separator are scarce, and a relationship is known to exist between trace element concentrations and particle size, it is important to know how effectively a cyclone can collect particles of various sizes. Although a cyclone's collection efficiency is case specific, the collection efficiency with respect to particle size for a "typical" cyclone is presented in Table 4-6. These data show that a typical cyclone can remove particles down to the 5 μm size range with relatively high efficiencies; however, the collection efficiency is significantly less for respirable particles (approximately 2 μm) and is relatively ineffective for particles in the 0.1-1.5 μm size range.

As was previously stated, data about a cyclone separator's ability to remove trace elements from the flue gas has not been well characterized; however, the trace element removal efficiency of a cyclone separator was calculated from data reported for a 250 MW power plant (33). The various

TABLE 4-6. TYPICAL CYCLONE PARTICLE COLLECTION VERSUS PARTICLE SIZE

Particulate Collection	
Particle Size (µm)	Typical Collection Efficiency[1] (%)
20	95
10	85
5	70
4	70
3	58
2	20-55
1.5	10-33
1.0	6-23
0.8	8-18
0.6	2-15
0.5	1-10
0.4	.5-7.5
0.3	.25-.45
0.2	.06-3.0
0.1	∿0-.5

[1] Low and high ends of range reflect expected collection of low and high efficiency cyclones, respectively.

Source: (17, 40, 42, 58)

trace elements for which data were reported and the collection efficiencies calculated are presented in Table 4-7.

4.3.1.3 Waste Streams Generated --

Operation of a cyclone separator results in a solid wastestream that must be disposed of. In many cases, this stream is combined with bottom ash from the combustion process and transported to a final treatment area such as an ash pond or a metal recovery process. In those cases where these ashes have been disposed of in an ash pond, the fly ash has been reported to form a gray scum on the pond's surface due to its buoyancy. This buoyancy is a result of the carbon dioxide trapped inside tiny silicate spheres that make up the fly ash (52). The gray scum can be controlled by skimming devices (23).

The pollutants in the flue gas exiting the cyclone are normally not at low enough levels to allow discharge of the gas into the atmosphere. In most cases making this effluent environmentally acceptable would require the removal of SO_2 and perhaps NO_x as well as further reduction of its particulate content.

4.3.2 Electrostatic Precipitator

4.3.2.1 Process Description --

The utility industry has utilized electrostatic precipitator (ESP) for more than 50 years to reduce particulate emissions, and they are still very popular in this industry (49, 53-55). This popularity has spread to other combustion processes such as municipal incineration and industrial boilers (1, 56-58). Operation of an ESP (Figure 4-14) is based on the generation of a high voltage, direct current corona. This corona is generated by a non-uniform electric field which occurs when a small diameter wire is used as one electrode and a plate or cylinder is used as the other electrode (53, 59). The corona ionizes the flue gases, and the ions become attached to the particles, thereby, charging them. The charged particles migrate toward the collection electrodes and are subsequently removed. Removal of the

TABLE 4-7. ACTUAL TRACE ELEMENT COLLECTION EXHIBITED BY A CYCLONE SEPARATOR

Trace Element	Collection Efficiency (%)
Total Ash	65.0
Aluminum	66.0
Antimony	7.4
Arsenic	75.3
Barium	95.4
Beryllium	84.3
Boron	31.4
Cadmium	44.0
Calcium	54.8
Chlorine	8.7
Chromium	27.7
Cobalt	45.1
Copper	56.8
Fluorine	25.3
Iron	54.2
Lead	30.0
Magnesium	61.0
Manganese	66.8
Mercury	3.2
Molybdenum	24.9
Nickel	18.6
Selenium	33.1
Silver	79.6
Sulfur	1.8
Titanium	74.4
Uranium	60.6
Vanadium	36.2
Zinc	39.4

Source: % Collection derived from (33)

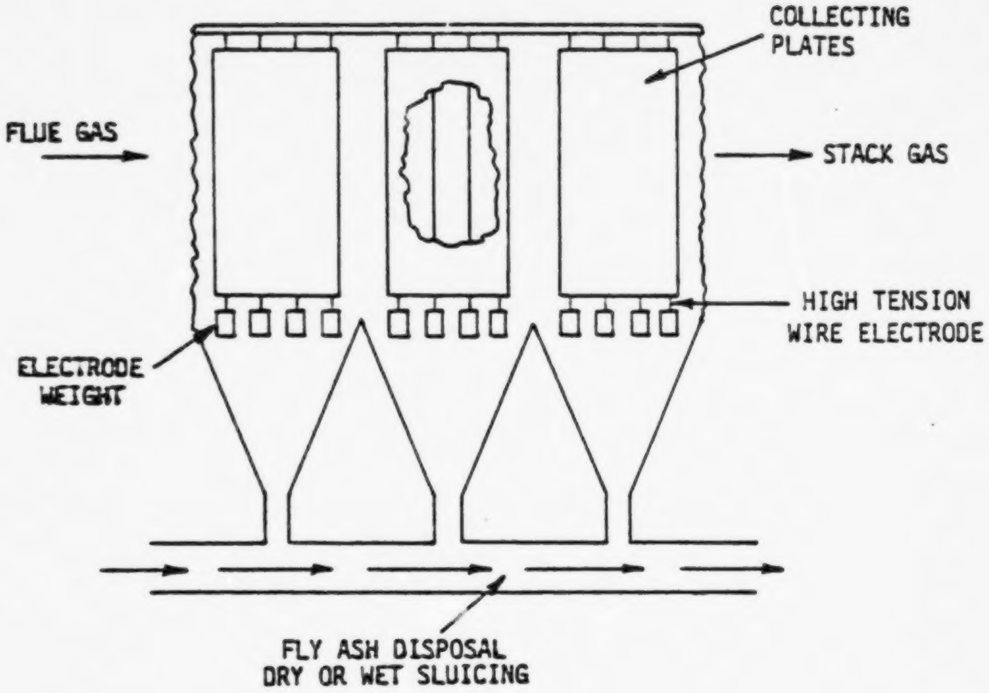

COLLECTING PLATES
FLUE GAS
STACK GAS
HIGH TENSION WIRE ELECTRODE
ELECTRODE WEIGHT
FLY ASH DISPOSAL DRY OR WET SLUICING

Figure 4-14. Plate-type electrostatic precipitator.
Source: (58)

accumulated dust may be achieved by washing the collection electrodes or rapping the electrodes to dislodge the dust, allowing it to drop into a hopper (48, 53). Major advantages of an ESP are their:

- relatively high collection efficiencies, with modern precipitators capable of achieving particulate efficiencies of greater than 99 percent, and
- relatively low pressure drop, which is particularly advantageous when large volumes of gases are handled (48, 53, 58).

The primary disadvantages of ESP's are the sensitivity of the collection efficiency to variations in fly ash resistivity or changing gas flow rates and the relatively high energy requirements (53, 58). Fly ash resistivity is very site and fuel specific, but generally the maximum in collection efficiency is for a fly ash resistivity of about 2 x 10^{10} ohm-cm. Fly ash with a higher resistivity ($<$2 x 10^{10} ohm-cm) reduces an ESP's collection efficiency; this type of ash is found in low sulfur coals. Lower resistivity ash, ($>$2 x 10^{10} ohm-cm) also decreases the collection efficiency of an ESP due to the easy reentrainment of this ash in the flue gas (53). The ash resistivity can be made more favorable by the addition of chemical agents (SO_3 or NH_3) to the flue gas, or operating the ESP at an elevated temperature as is shown in Figure 4-15 (50, 53, 60-62).

This elevated temperature concept is the basis of the "hot" electrostatic precipitator. The hot ESP is located ahead of the air heaters instead of in its normal downstream position (cold ESP) (60). Although the hot ESP operates at a condition of optimum ash resistivity, Thoem reports results of a study that indicate that for a given total particulate control efficiency, a cold ESP appears to be a better fine particulate and therefore trace element collector than the hot ESP (61). The cold ESP also has the advantage of handling a smaller volume of gas because a gas at 150°C is about 25 percent less in volume than the same gas at 315°C (60). Mesich et al. compared the total particle collection efficiencies of hot-side and cold-side ESP's; their results showed that there was no difference in the collection efficiencies of these ESP's (63).

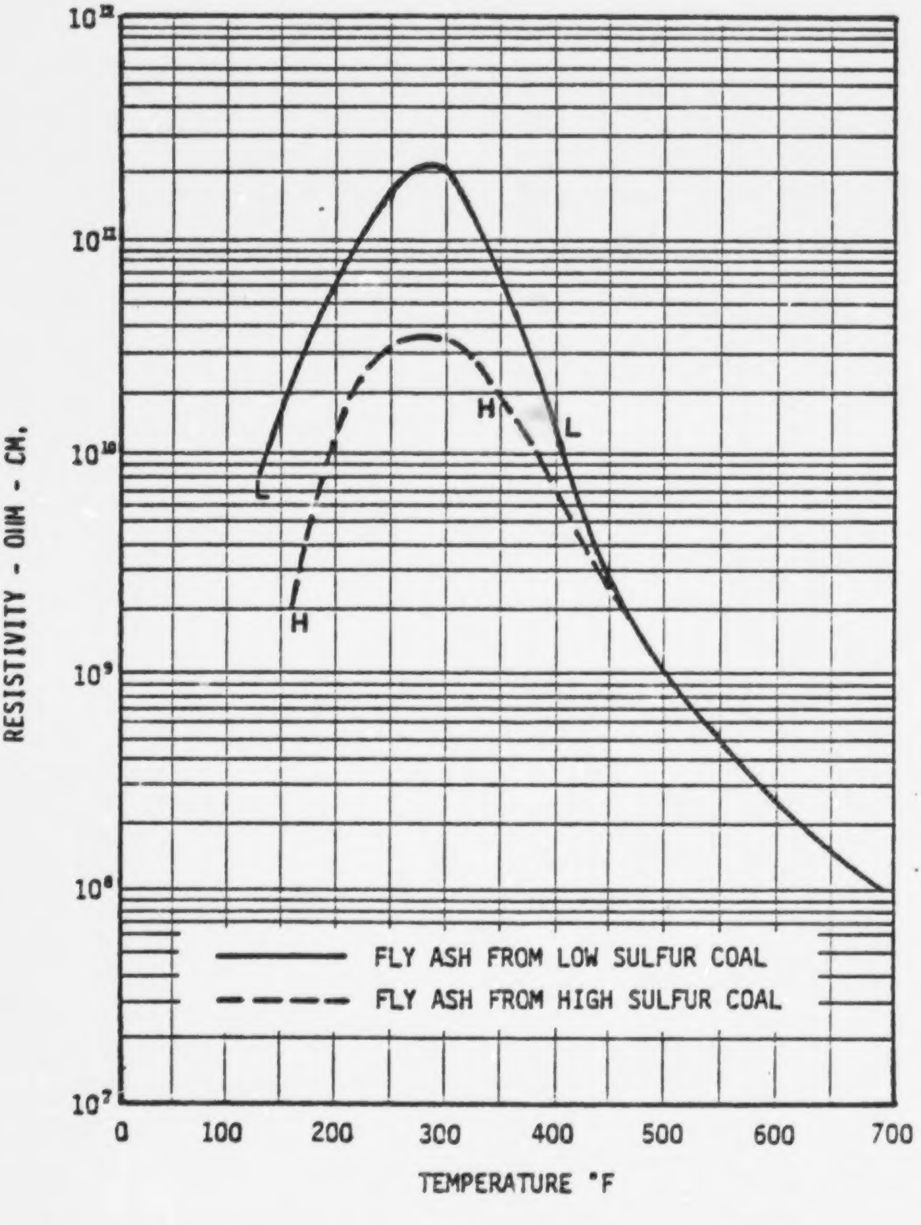


Figure 4-15. Fly ash resistivity variations with temperature.
Source: (53)

4.3.2.2 Trace Element Collection Efficiency --

The ability of an electrostatic precipitator to collect particles and trace elements condensed on fly ash particles is highly dependent on particulate size. Several investigators have studied the impact of particulate size on ESP collection efficiency; their results are graphically summarized in Figure 4-16 (17, 64-68). From these data it is apparent that these researchers did not consider submicron particles; however, control of submicron particles was considered in studies by Shannon et al. and Ondov et al. (41, 69). The results of these studies are in good agreement and are summarized in Table 4-8. Although the data in this table indicate that ESP's exhibit high collection efficiencies for submicron particles, Paulson et al. reported that when the proportion of particles smaller than 5 µm reached a level that exceeded 45 percent (by weight), the ESP collection efficiency was unacceptably low (less than 98.5 percent) (70).

Like other control technologies, little data regarding the ability of an ESP to control trace element emissions from combustion processes are available; however, sufficient data to allow the calculation of the trace element removal efficiencies of four commercial-scale ESP's have been reported. These ESP's were utilized in facilities that varied in size from 105 MW to 625 MW. The trace element collection efficiencies calculated for the ESP's at the various facilities are presented in Table 4-9. Although some differences in the calculated efficiencies could be expected due to differences in the operation of the utility plants or the ESP's or their respective design capabilities, in many cases these efficiencies were in relatively good agreement.

4.3.2.3 Wastestreams Generated --

Two streams that are of concern exit ESP's. The first stream is the collected fly ash. Since this effluent is the same as the ash discharged from a cyclone separator, it can be disposed of in the manner discussed in Section 4.1.6. The second stream is the effluent flue gas, which contains SO_2 and NO_x. In most cases, the level of these contaminants must be reduced before the flue gas can be discharged to the atmosphere.

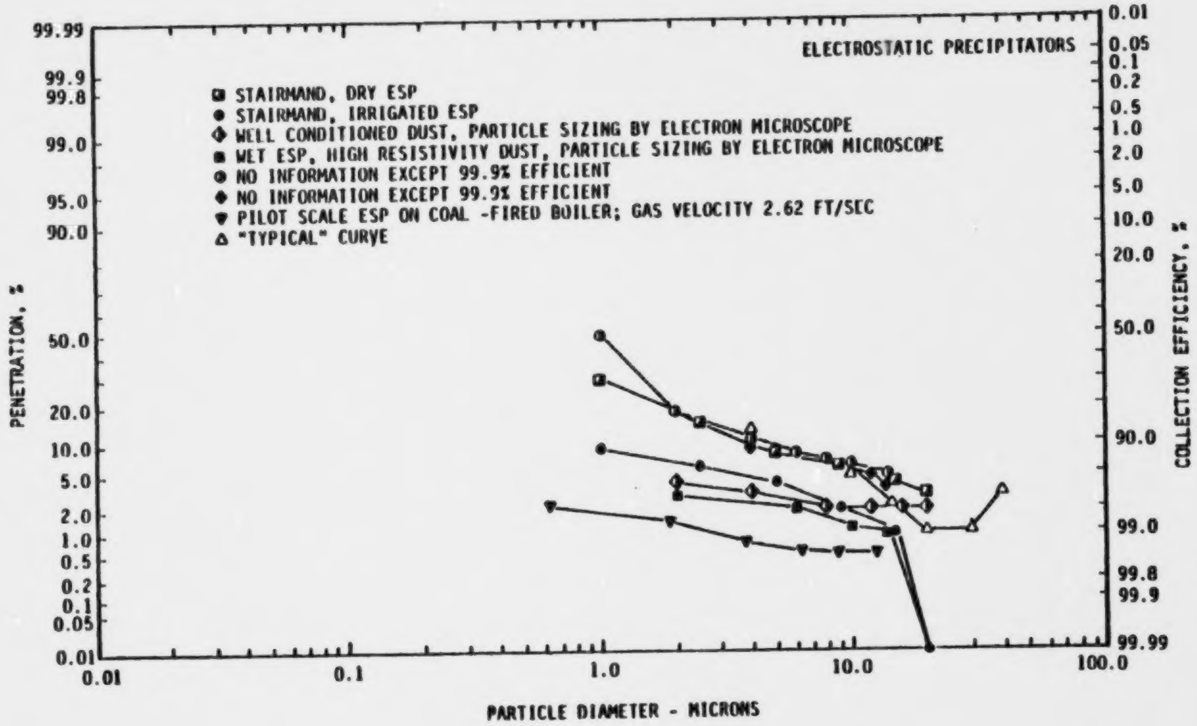


Figure 4-16. Fractional efficiency data for electrostatic precipitators.

Source: (17)

TABLE 4-8. PARTICLE COLLECTION EFFICIENCY EXHIBITED BY AN ESP (COLD-SIDE)

Particle Size (μm)	ESP Collection Efficiency (%)
20	>99.9
10	>99.9
5	99.7
4	99.7
3	99.2
2	98.0
1.5	97.0
1.0	96.0
0.8	94.0
0.6	93.0
0.5	92.0
0.4	90.0
0.3	92.0
0.2	96.0
0.1	97.0
0.05	94.0
0.01	90.0

Source: (41,69)

TABLE 4-9. TRACE ELEMENT COLLECTION EFFICIENCY OF ESP'S AT SEVERAL COAL-FIRED POWER PLANTS

		ESP Collection Efficiencies (%)		
Trace Elements	Plant A	Plant B	Plant C	Plant D
Aluminum	99.2	ND	99.6	98.9
Antimony	96.0	99.1	77.5	92.3
Arsenic	99.9	ND	97.5	88.5
Barium	99.9	ND	99.5	96.0
Beryllium	97.6	ND	ND	99.1
Boron	94.7	ND	ND	ND
Bromine	ND	ND	ND	99.8
Cadmium	95.5	98.8	96.7	91.2
Calcium	99.0	ND	99.6	98.7
Cerium	ND	ND	99.4	98.7
Cesium	ND	ND	99.0	98.8
Chlorine	4.5	ND	ND	ND
Chromium	85.6	99.8	98.6	96.2
Cobalt	98.2	ND	99.3	97.5
Copper	99.1	ND	99.3	ND
Dysprosium	ND	ND	ND	98.6
Euroqium	ND	ND	99.6	98.7
Fluorine	92.3	ND	ND	ND
Gallium	ND	ND	100.0	95.6
Hafnium	ND	ND	99.3	98.7
Inqium	ND	ND	ND	94.6
Iron	98.6	99.6	99.3	98.7
Lead	91.6	99.3	96.6	94.5
Lanthanum	ND	ND	99.3	98.7
Lutetium	ND	ND	ND	98.6
Magnesium	99.0	ND	100	98.8
Manganese	98.6	100	99.1	98.4
Mercury	0.0	ND	ND	ND

(continued)

TABLE 4-9. CONTINUED

Trace Elements	Plant A	ESP Collection Efficiencies (%) Plant B	Plant C	Plant D
Molybdenum	89.2	ND	ND	94.9
Neodynium	ND	ND	ND	98.7
Nickel	78.5	99.7	99.4	ND
Potassium	ND	ND	99.4	99.0
Rubidium	ND	ND	99.4	94.5
Samarium	ND	ND	99.6	98.6
Scandium	ND	ND	99.5	98.5
Selenium	61.8	94.3	95.7	92.3
Silver	98.7	ND	ND	ND
Strontium	ND	ND	100	ND
Tantalum	ND	ND	99.3	98.7
Terbium	ND	ND	ND	98.6
Thorium	ND	ND	99.3	98.7
Titanium	99.2	ND	99.1	98.5
Tungsten	ND	ND	ND	92.8
Uranium	98.2	ND	98.6	96.3
Vanadium	92.2	99.9	98.7	96.3
Ytterbium	ND	ND	ND	98.7
Zinc	96.3	99.6	98.2	93.7
Zirconium	ND	ND	ND	98.6
Total Ash	99.1	99.7	99.5	97.0

ND - No data.

Bases:
1) Plant A - 350 MW unit with hot-side ESP; source: (40)
2) Plant B - 105 MW unit; source: (73)
3) Plant C - 290 MW unit; source: (19)
4) Plant D - 625 MW unit, source: (27)

4.3.3 Wet Scrubbers

4.3.3.1 Process Description --

Wet scrubber technology has been widely used to control gaseous (SO_2, NO_x) and particulate emissions from combustion processes (1, 17, 53, 71, 72). This technology is made up of four basic types of scrubber: cyclone, venturi, spray tower, and packed bed, or variations of these scrubbers (53). The cyclone and venturi are best suited to remove particulates from the flue gas, while turbulent contact scrubbers like the spray tower and packed bed scrubbers are used principally to control gaseous pollutants (48, 53, 73). Regardless of its primary function, a wet scrubber can be expected to reduce, to some degree, the level of trace element emissions from the combustion process on which it is utilized (47).

4.3.3.2 Particle Scrubbers --

The cyclone and venturi scrubbers have been used primarily to remove particles from the flue gas. These scrubbers characteristically exhibit relatively high flue gas pressure drops as well as high energy requirements. Wet cyclone scrubbers can have several configurations; however, in each configuration the gas is set into rotary motion by being tangentially introduced into the scrubber or by vanes in the scrubber (53). The particles adhere to the liquid droplets and both are forced to the vessel's walls by centrifugal forces (48, 53). The liquid is discharged at the bottom, and the "clean" gas exits at the top. An illustration of a wet cyclone scrubber is presented in Figure 4-17. Typical liquid-to-gas ratios in cyclone scrubbers range from about 5 to 15 gallons/1000 actual cubic feet of gas (48). Collection efficiency is typically 96 percent for 2-3 μm particles at a pressure drop of 1.3-2.3 inches of water (53). The primary advantages of a wet cyclone separator are its enhanced particulate collection due to the addition of a liquid, and its simplicity. Disadvantages associated with the cyclone scrubber include: (1) increase in a plant's water and utility requirements (2) significantly increased energy consumption when higher removal efficiencies are desired, and (3) generation of a wastewater (48, 53).

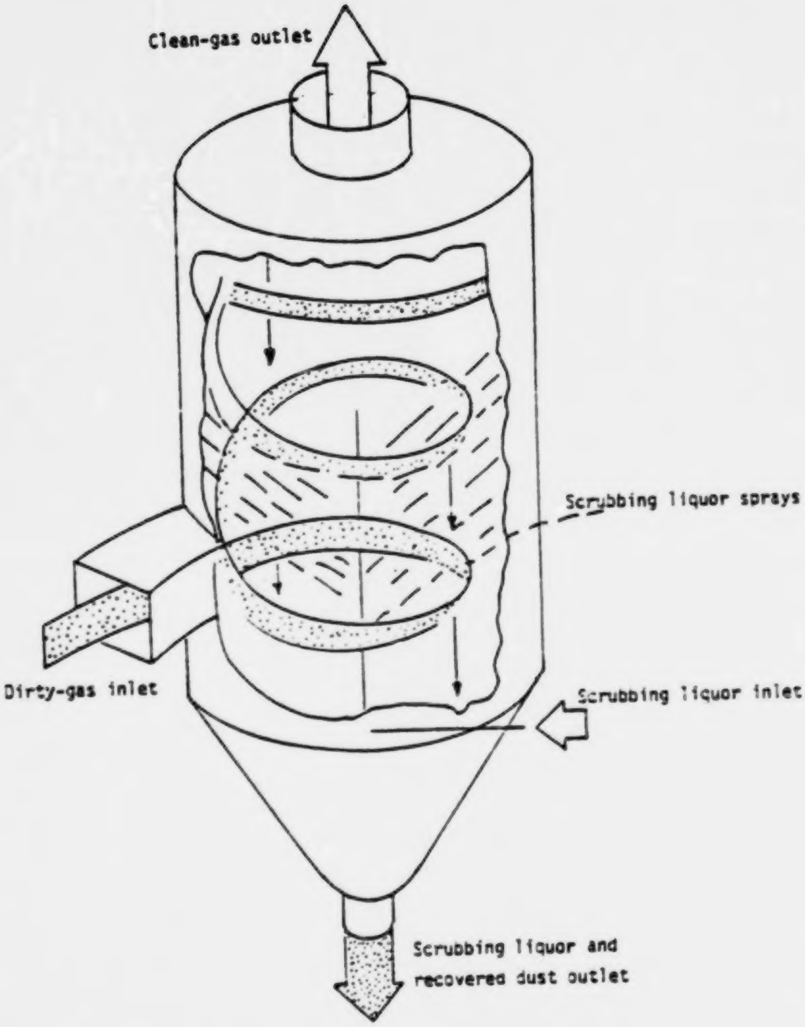

Clean-gas outlet
Scrubbing liquor sprays
Dirty-gas inlet
Scrubbing liquor inlet
Scrubbing liquor and
recovered dust outlet

Figure 4-17. Diagram of cyclone scrubber.
Source: (48)

Venturi scrubbers are often used when very high collection efficiencies are required and where most of the particulates are smaller than 2 μm in diameter (71). The venturi-type scrubber (Figure 4-18) achieves a relatively high collection efficiency by introducing the scrubbing liquid at right angles to the high velocity gas flow in the venturi throat. Gas in the throat of a venturi typically attains a velocity of 200-600 ft/sec (53). The velocity of the gases alone causes the atomization of the liquid. When the venturi scrubber is primarily used to remove particles, it may be placed in a vertical arrangement. This arrangement is claimed to produce turbulent mixing of gas and liquid which results in a lower scrubbing liquor requirements, as well as a lower pressure drop (53). Liquid rates for this type of scrubber typically range from 5-20 gallons per thousand actual cubic feet of gas. Gas-side pressure drop in venturis typically ranges from 5-15 inches of water (48). Venturi scrubbers are capable of over 99 percent removal of particles that are 2-5 μm in size (40, 48). Primary advantages of venturi scrubbers are their relatively high removal efficiencies for smaller particles and ability to remove particulate and gaseous pollutants without requiring any physical modification. A venturi's main disadvantage is the relatively high pressure drop and the corresponding energy requirement necessary to attain a high removal efficiency. As with any wet collection device, a wastewater is generated by a venturi scrubber.

4.3.3.3 Gas Scrubbers --

A schematic of a turbulent contact (spray tower) scrubber is presented in Figure 4-19. In this type of scrubber, liquid is sprayed into the top of the scrubber. The falling droplets encounter a countercurrent flow of gas and collect particles by impaction and interception. Because of its relatively low particle collection efficiency, this type of scrubber is primarily used to remove gaseous pollutants (53). The primary advantages exhibited by this scrubber are its:

- simplicity,
- dual removal of gaseous and particulate pollutants,
- relatively low pressure drop and corresponding low energy requirements,

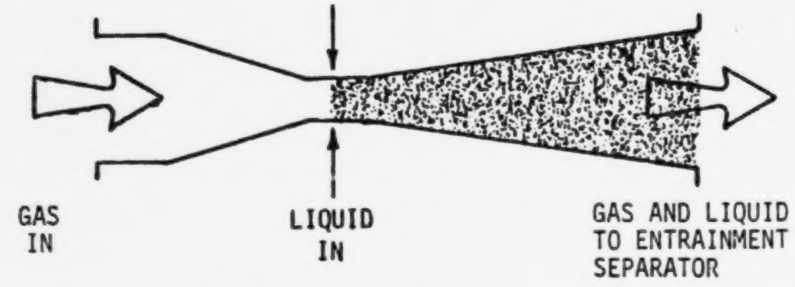

GAS
IN
LIQUID
IN
GAS AND LIQUID
TO ENTRAINMENT
SEPARATOR

Figure 4-18. Schematic of venturi scrubber.
Source: (53)

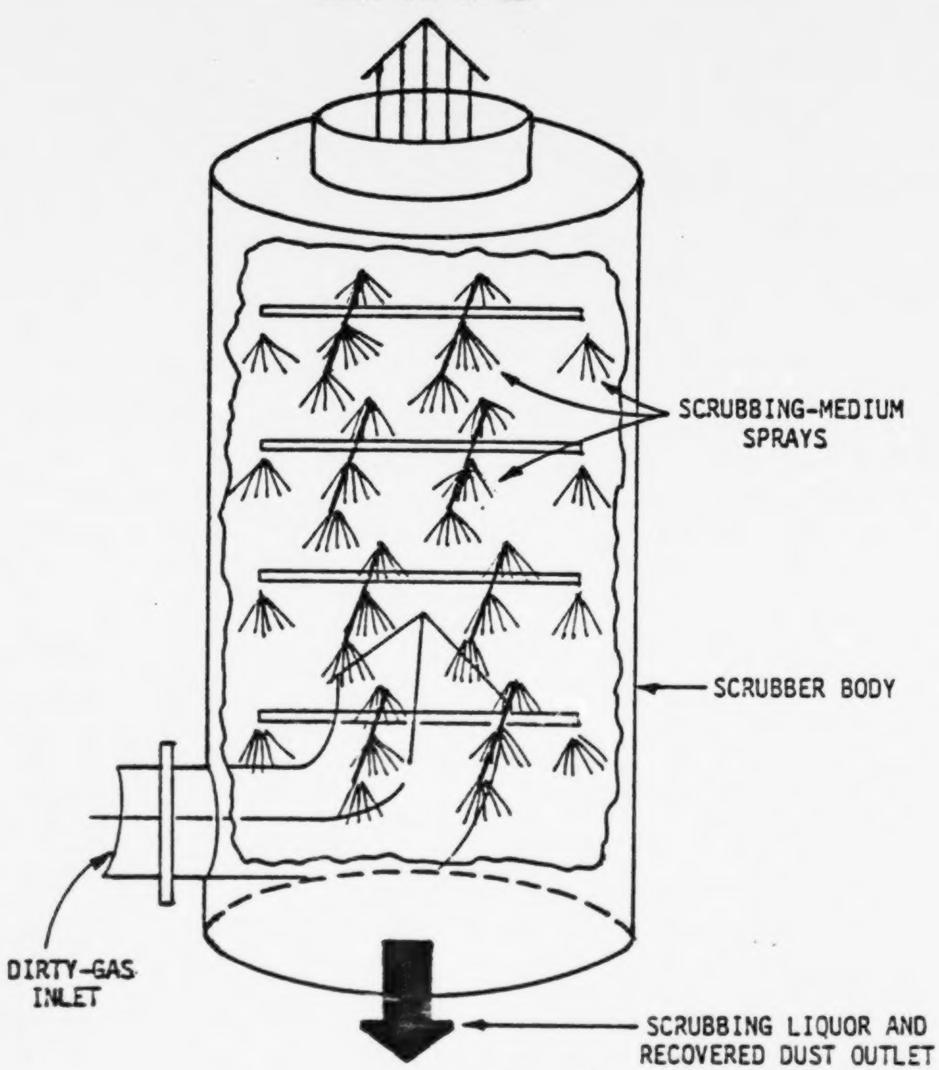

CLEAN-GAS OUTLET
SCRUBBING-MEDIUM SPRAYS
SCRUBBER BODY
DIRTY-GAS INLET
SCRUBBING LIQUOR AND RECOVERED DUST OUTLET

Figure 4-19. Schematic of spray tower scrubber.
Source: (48)

- minimization of dust reentrainment, and
- ability to be retrofitted to an existing plant.

Disadvantages associated with this scrubber are:

- relatively low collection efficiency of small particles,
- significantly high power requirements associated with increased collection efficiencies,
- potential requirement of a mist eliminator due to significant liquid entrainment, and
- generation of a wastewater that must be treated before it can be reused or discharged (48, 53).

4.3.3.4 Trace Element Collection Efficiency --

As with other control devices, the ability of a wet scrubber to reduce trace element emissions is expected to be correlated with its efficiency for removal of small particles. Shannon summarized collection efficiency versus particle size data from a number of sources for various wet scrubbers (17). His results are shown in Figure 4-20. Three studies have considered the impact of wet scrubbers on trace elements emitted from coal-fired utility boilers. Trace element collection efficiencies were calculated from this data and are presented in Table 4-10.

TRW, Inc. conducted some tests in which the ability of a pilot-scale flue gas desulfurization scrubber to control trace element emissions from a boiler that could be fired with coal or fuel oil was measured (20). The trace element removal efficiencies exhibited by this scrubber are delineated in Table 4-11 on the basis of the type of fuel fired in the boiler. These data show that the trace element removal efficiency of an SO_2 scrubber which is applied to a coal-fired boiler is comparable to the removal efficiencies exhibited by a particulate scrubber such as a venturi. The removal efficiencies of the SO_2 scrubber are generally lower for the oil-fired application than for the coal-fired case. These results reflect the smaller sizes of particles from the oil-fired boiler, and the subsequent difficulty involved in capturing these particles (20).

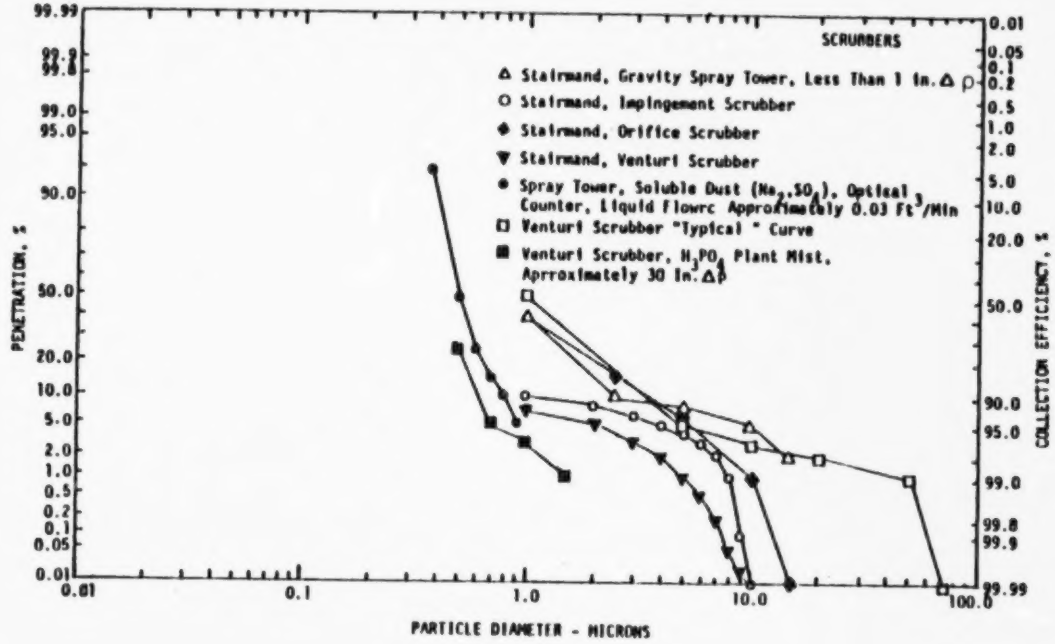


Figure 4-20. Fractional efficiency data for wet scrubbers.

Source: (17)

TABLE 4-10. COLLECTION EFFICIENCIES EXHIBITED BY VARIOUS WET SCRUBBERS FOR TRACE ELEMENTS DISTRIBUTED ON FLY ASH

Trace Elements	Collection Efficiencies (%) Venturi (1) Scrubber	 Venturi (2) Scrubber	 Horizontal (3) Scrubber
Al	99.5	99.7	ND
Ag	ND	94.8	ND
As	96.3	92.1	98.0
B	ND	93.6	ND
Ba	99.5	99.0	6.0
Be	ND	99.2	55.0-82.0
Br	ND	ND	ND
Ca	99.7	99.0	99.6
Cd	ND	92.3	46.0
Ce	> 99.9	ND	ND
Cl	98.4	ND	ND
Co	> 99.8	96.9	ND
Cr	96.1	88.9	ND
Cs	> 99.9	ND	ND
Cu	ND	99.3	ND
Dy	> 99.9	ND	ND
Eu	> 99.9	ND	ND
F	ND	98.0	98.9
Fe	> 99.9	99.2	ND
Ga	99.5	ND	ND
Hf	> 99.9	ND	ND
Hg	ND	12.6	22.2
In	99.3	ND	ND
K	> 99.9	ND	ND
La	> 99.9	ND	ND
Lu	> 99.9	ND	ND
Mg	99.9	98.5	ND

(continued)

TABLE 4-10 . CONTINUED

Trace Elements	Collection Efficiencies (%)		
	Venturi (1) Scrubber	Venturi (2) Scrubber	Horizontal (3) Scrubber
Mo	98.4	52.8	92.2-95.8
Mn	99.2	99.6	ND
Na	99.9	ND	ND
Nd	> 99.9	ND	ND
Ni	ND	95.0	90.8-98.0
Pb	ND	98.0	62.8-97.1
Rb	ND	ND	ND
S	ND	37.8	ND
Sb	95.5	99.3	83.0-50.0
Sc	> 99.9	ND	ND
Se	85.0	97.8	60.9-79.0
Sm	> 99.9	ND	ND
Sr	99.8	ND	ND
Ta	> 99.9	ND	ND
Tb	ND	ND	ND
Th	> 99.9	ND	ND
Ti	> 99.9	99.6	99.2
U	99.5	96.0	ND
V	99.2	97.0	89.0
W	97.4	ND	ND
Yb	> 99.9	ND	ND
Zn	99.3	97.4	ND
Zr	> 99.9	ND	ND

ND - No Data

(1) Source: (34) (2) Source: (32)
(3) Data questionable because scrubber had not attained steady state operation. Horizontal scrubber is similar in some respects to spray tower; However, it has a lower power consumption. Source: (75)

TABLE 4-11. COMPARISON OF TRACE ELEMENT REMOVAL EFFICIENCIES OF AN SO_2 SCRUBBER ON A COAL OR FUEL-OIL FIRED BOILER

	Removal Efficiencies (%)	
Trace Element	Fuel Oil-Fired Boiler	Coal-Fired Boiler
Be	Unknown	98
Hg	87	55
Ca	83	99
Mg	91	99
Sb	91	99
As	81	97
B	93	88
Cd	77	99
Cr	90	95
Co	89	99
Cu	99	99
Fe	95	99
Pb	94	99
Mn	87	98
Mo	89	99
Ni	83	95
V	71	98
Zn	90	98
Se	87	97
Sr	98	99
Al	92	99
Zr	94	99
Total	87	99

NOTE: SO_2 scrubber is a double alkali unit.

Source: (20)

4.3.3.5 Wastestreams Generated --

The operation of any wet scrubber results in the generation of an aqueous wastestream. If particulate scrubbing is the only function performed, the wastestream will be a wastewater containing suspended solids. This stream can be combined with the bottom ash and treated or disposed of accordingly. If SO_2 is the primary function of the scrubber and the scrubbing process is a "throwaway" system, a sludge is generated. The waste sludge, which is approximately 55-60 percent solids and represents the largest volume of solid waste generated by a coal- or oil-fired power plant, is sent to an evaporative pond (usually with the bottom ash and fly ash slurries) or mechanically dewatered. In many cases the solids are ultimately used as landfill (2, 4, 7).

Spent scrubber sludges principally contain calcium sulfate, calcium sulfite, sodium chloride, magnesium chloride, as well as detectable quantities of trace elements (2, 7, 74). Disposal of these sludges in temporary or permanent ponds or landfills may result in contamination of groundwaters and is, therefore, of concern. In many cases, utilities minimize the potential contamination of groundwaters by lining the disposal pond with an impervious liner (4, 75). Holland, _et_ _al_. tested the leachability of trace elements from waste sludges in unlined ponds (76). These researchers used waste sludges from five operating power plants and found that selenium, boron, and chromium pose the greatest threat to groundwaters; however, they also found that typical soils can protect groundwaters to some degree from selenium, boron, and chromium contamination. Clay was found to prevent the occurrences of any contamination, while sandy soils provided the least protection.

4.3.4 Baghouses (Fabric Filters)

4.3.4.1 Process Description --

Although baghouses have not been widely utilized to control particulate emissions from coal-fired utility boilers in the past, it has been estimated that U.S. utilities will spend five billion dollars for baghouse systems by 1985 (77, 78). This projected use of baghouses reflects the anticipated extensive use of low sulfur, high-ash coal as well as the need to achieve greater control of particulate emissions. The first full-scale baghouse application to a coal-fired power plant was installed at the Sunbury Steam Electric Company in 1973 (79). Currently, several plants use baghouses to control particulate emissions. These companies, the type fuels and boilers used, as well as the capacities of their baghouses are summarized in Table 4-12 (80). It has also been reported that the largest power plant in the U.S. (Shawnee Power Plant in Kentucky) has committed \$80 x 10^6 for the installation of 10 baghouse units (81).

A baghouse (Figure 4-21) removes particles by filtering the gas through a fabric. As the dust cakes the fabric surface, the collection efficiency of the baghouse increases. However, the pressure drop through the baghouse also increases until it reaches a point where the fabric must be cleaned. Baghouses are normally classified by the techniques employed to clean the fabric. The shaker-type baghouse is supported by a structural framework which is free to oscillate when driven by a small electric motor. Periodically, one compartment is isolated so that no gas flows through it. During this time, the isolated compartment is shaken for a specified period of time to dislodge the cake into the hopper below.

In the reverse-flow type baghouse, individual compartments are again isolated and an auxiliary fan forces air through the bags in the direction opposite to the normal flow of gas. When the bag is reinflated, the cake is dislodged and falls into the hopper. Reverse jet baghouses employ a manifold which surrounds the bag and travels the length of the bag in a cycle. A jet of high pressure air is shot from the manifold and blows the dust off the filter.

In the reverse pulse type baghouse, a short pulse of compressed air is sent through a venturi directed from the top to bottom of the filter. The resulting air mass expands the bag and removes the dust cake (82).

Some of the more important design considerations for baghouses are: (1) air-to-cloth ratio (filtering velocity), (2) filter drag, and (3) pressure drop. The following sections discuss in detail the operating principles, applicability, design considerations, and operating costs for fabric

TABLE 4-12. BAGHOUSE INSTALLATIONS

Case No.	Plant and Location	Fuel	Fuel Firing Equipment	Plant Capacity on Baghouses †
1	Alamitos, CA	No. 6 Oil 1.5-1.7% S	Tangential tilting return flow burners	2,305,000 lb/hr
2	Sunbury Shamokin, PA	0.8% S anthracite and up to 6% S petroleum coke (75/25 mixture)		175 MW
3	Carborundum Niagara Falls, NY	Bituminous Coal 7% ash 2.3% S	Spreader	75,000 lb/hr
4	Amal. Sugar NYSSA, OR	Coal	Spreader	200,000 lb/hr
5	Amal. Sugar Nampa, ID	Coal		150,000 lb/hr
6	Colorado UTE	0.6-1.9% S Coal 12% ash	Spreader	3 units each 132,000 lb/hr
7	Holtwood, PA	Anthracite, fines and petroleum coke	Pulverized coal	50% of 80 MW unit
8	Winston-Salem, NC	0.8% S Coal	Spreader	75,000 lb/hr
9	Winston-Salem, NC	0.8% S Coal	Spreader	40,000 lb/hr
10	du Pont	Coal	Spreader	
11	du Pont	Coal	Spreader	

Source: (80)

† Capacity rated in either megawatts (MW) of electrical power or pounds per hour lb/hr) of steam.
Source: (80)

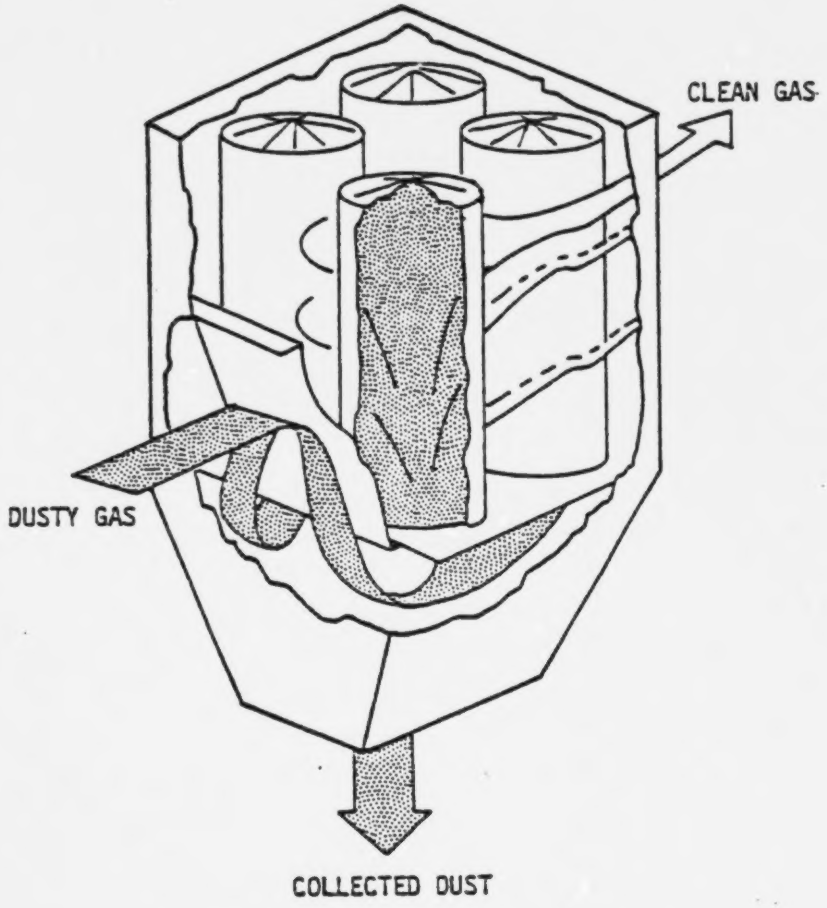

CLEAN GAS
DUSTY GAS
COLLECTED DUST

Figure 4-21. Fabric filter (collection outside bags).
Source: (55)

filters (82). The primary advantages of baghouses are their high collection efficiencies for small (submicron) particles and insensitivity to changes in coal ash content or ash characteristics (48, 53, 77, 79). Major disadvantages of baghouse control devices are the temperature and chemical limitations of fabrics that have been used, relatively short life of the filter fabrics used and relatively high pressure drop and correspondingly high energy requirements (19, 48, 80).

4.3.4.2 Particle Collection Efficiency--

Unlike most of the control devices that have been previously discussed, baghouses are capable of controlling submicron particles with approximately 99 percent efficiency. The differences between the collection efficiencies exhibited by baghouses and other control devices for small particles are largely due to the mechanisms that control the collection of these particles (81). The collection of the larger particles (>1 μm) is controlled by impaction and electrostatic attraction, while Brownian diffusion becomes the controlling factor for particles that are smaller than 0.2 μm (40, 81).

Brownian diffusion is proportional to gas velocity and will, consequently, be dependent in a baghouse on the air-to-cloth ratio (48, 88). The air-to-cloth-ratio relates the volume of flue gas to the surface area of the filter fabric. The impact of this ratio on the collection efficiency of particles ranging in size from 0.1 to 10 μm is illustrated in Figure 4-22. Based on a pilot plant test, McKenna *et al*. (81) reported the particulate collection efficiencies presented in Table 4-13.

TABLE 4-13. DUST REMOVAL EFFICIENCIES OBTAINED DURING PILOT PLANT TESTS

Nomex Felt Filter Media With Air-to-Cloth Radio of 2/6

Particle Diameter	Removal %
<9.5	99.84
6	99.74
4	99.78
2.8	99.69
1.75	98.03
0.9	99.21
0.54	99.16
0.36	96.88
<0.36	98.98

Source: (81)

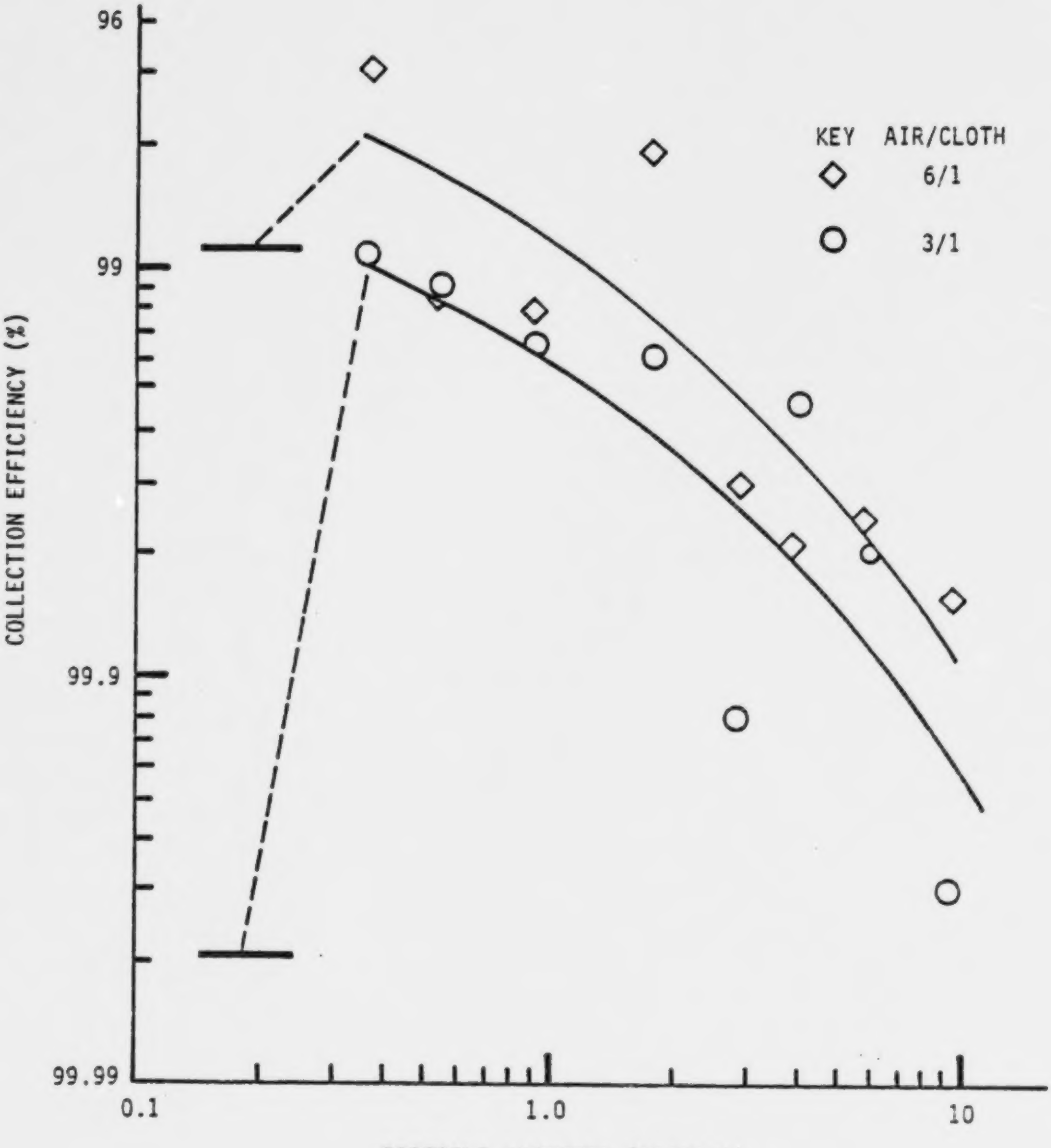


Figure 4-22. Fabric filtration collection efficiency vs particle diameter.

Source: (81)

The particulate collection efficiencies of a commercial-scale baghouse that is being utilized at the Nucla Power Plant (a western coal-fired spreader stoker power plant) are presented graphically in Figure 4-23. As this figure shows, the baghouse's median overall collection efficiency was consistently above 99.4 percent; there is, however, an obvious lack of data regarding the collection efficiency of submicron particles.

4.3.4.3 Trace Element Collection Effiency --

Data reflecting the trace element collection efficiency of a baghouse is very limited. Yeh _et al_. reported that a baghouse was superior to an ESP in reducing toxic trace element emissions from a coal-fired combustion (83). In this study, the collected fly ash and slag retained an average of 91 percent of arsenic in the coal, 77 percent of the Be, 55 percent of the Cd, 82-100 percent of the Hg, 63 percent of the Pb, and 87-100 of the Se at optimum conditions. Additional trace element collection data was obtained from application of baghouses at a coal-fired power plant and steel mill (46, 73). These collection efficiencies are presented in Table 4-14.

TABLE 4-14. TRACE ELEMENT COLLECTION EFFICIENCIES EXHIBITED BY BAGHOUSE COLLECTORS (% REMOVAL)

Trace Element	POWER PLANT		Steel Mill
	11 MW Load	12 MW Load	
Al	100	100	--
Ca	100	100	--
Cr	—	—	99.9
Cu	—	100	100
Fe	>99.9	100	—
Mn	—	--	99.8
Pb	>99.9	100	—
Ni	—	100	100
S	>99.9	55.2	—
Si	100	100	—
Ti	100	100	--
U	—	—	100
Zn	100	100	—

Source: (31, 46)

4.3.4.4 Wastestreams Generated --

Two wastestreams exit the baghouse, the collected fly ash and flue gas. Collected fly ash will contain those trace elements that are condensed on

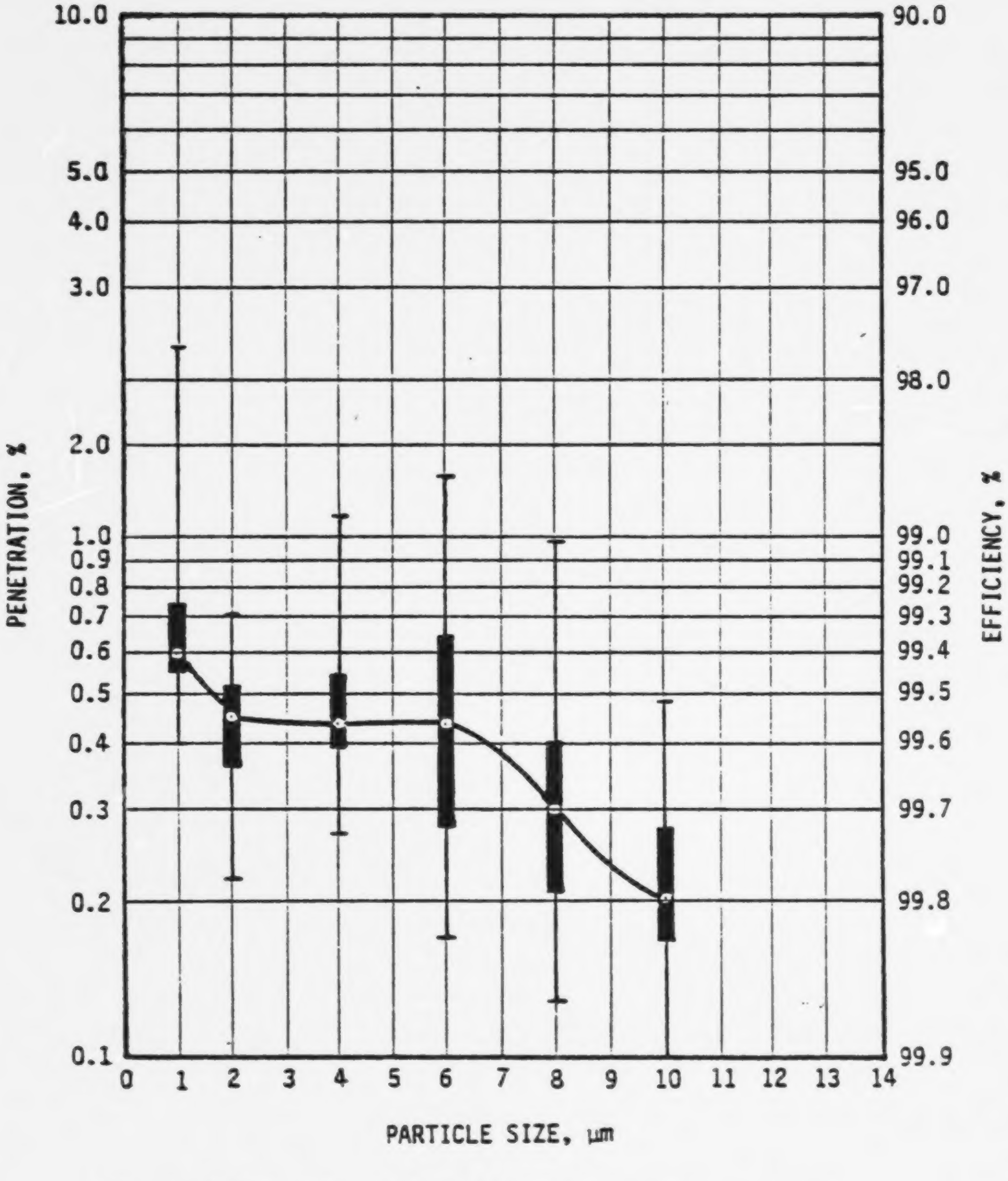


Figure 4-23. Median fractional efficiency for 22 tests.

Source: (45)

the fly ash. Because this stream is dry, it may be an excellent source for the recovery of valuable metals (9, 43). However, the economics of this procedure may be prohibitive and must be carefully analyzed. In a typical facility, the collected ash is combined with boiler bottom ash and sent to a final disposal process (4). The flue gas normally contains relatively little fly ash; however, the gas could contain significant levels of gaseous pollutants. The levels of these pollutants might require further reduction before the flue gas could be discharged to the atmosphere.

4.3.5 Anticipated Future of Trace Element and Fine Particulate Control Processes

McIlvaine reported in a study to the EPA that 66,000 Mw of high sulfur coal burning boilers and 67,000 Mw of low sulfur coal burning boilers will be ordered by 1982 for installation by 1985(81). Because low sulfur coal has a relatively high ash content and high ash resistivity (which makes use of electrostatic precipitators difficult), baghouses are expected to be utilized in 45 percent of these facilities, either singly or combined with another control process (such as an SO_2 scrubber). It has also been estimated that baghouses will not be used in any of the future high sulfur, low ash installations. Precipitators are anticipated to be used in 45 percent of the low sulfur facilities and 85 percent of the high sulfur installations. Wet particulate scrubbers will be used for 10 percent of the low sulfur installations and 15 percent of the high sulfur installations. In addition to new units, about 8,000 Mw yearly of existing capacity will have to be brought into compliance with particle regulations; of these retrofitted installations, 20 percent are expected to be baghouses, 10 percent scrubbers, and 70 percent ESP's. A summary of these projections for future use of control processes is presented in Table 4-15. The predicted increase (based on installed costs) of particulate control equipment in the utility sector from 1976 to 1982 is depicted in Figure 4-24. Overall, in the industrial and utility sectors, it is predicted that between 1976 and 1982 the total air pollution control equipment market will increase 500 percent - from 1.7 to 5.2 billion dollars (81).

TABLE 4-15. ESTIMATED FUTURE USE OF VARIOUS CONTROL PROCESSES

	New Installations Low Sulfur (67,000MW)	New Installations High Sulfur (66,000MW)	Retrofit Installations (8,000MW)
ESP's	45%	85%	70 %
Baghouses	45%	0%	20 %
Wet, Particle Scrubbers	10%	15%	10 %

Source: (81)

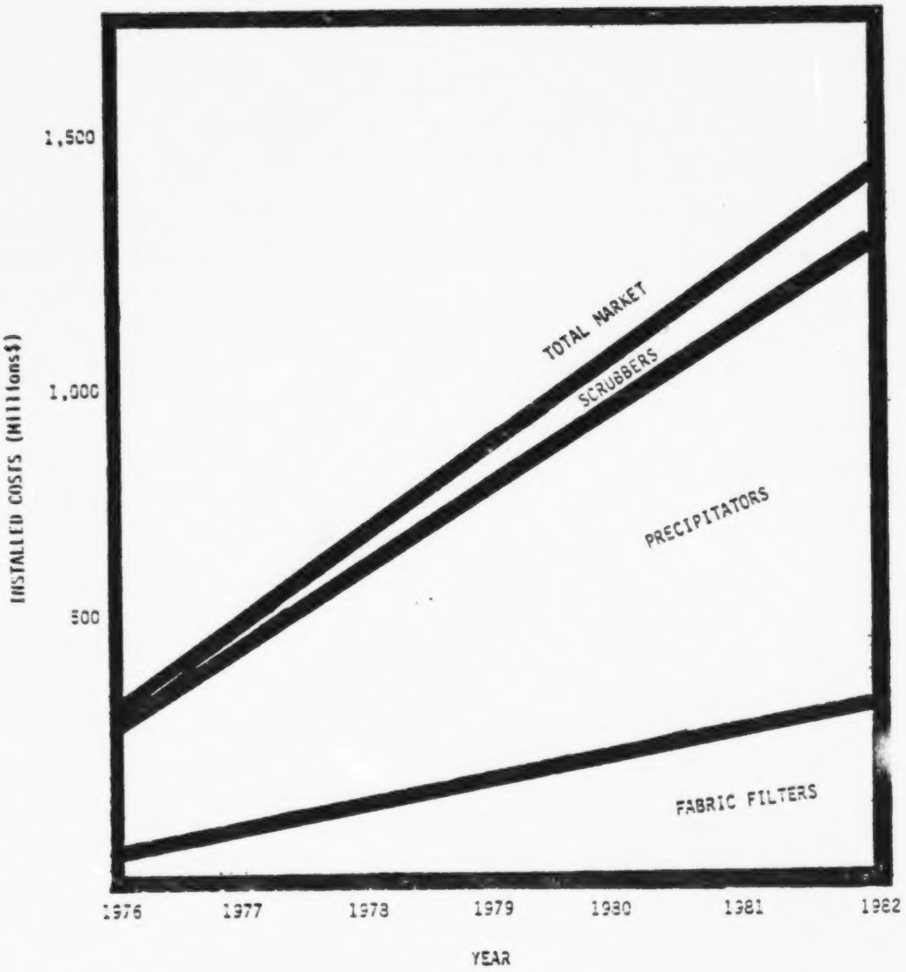


Figure 4-24. Anticipated use of various particulate control devices in the utility industry.

Source: (81)

4.4 COST OF FINE PARTICULATE AND TRACE ELEMENT CONTROL PROCESSES

Since it has been speculated that baghouses, ESP's, and particulate scrubbers will be used extensively by the utility industry for particle control, it is germane to examine and compare the costs associated with these devices.

4.4.1 Baghouse Costs

Although baghouses are currently being used in the utility industry on a commercial scale and are expected to become more popular for controlling particles, little cost information is available for this control device. The capital costs of baghouses are dependent on the filter media used and the air-to-cloth ratio. Mycock estimated the installed costs of a baghouse designed to handle a 150,000 ACFM slipstream from a 250,000 lbs/hr pulverized coal boiler (81). These costs were developed for three different filter media and air-to-cloth ratios on the bases of actual bag manufacturer quotes obtained in 1978. Table 4-16 shows the costs of the bags as a percentage of the installed costs.

TABLE 4-16. BAG COST AS A PERCENT OF INSTALLED COST

Filter Media	Installed Cost ($)	Bag Cost ($)	% of Installed Cost Due to Bag Cost
Woven Glass			
2/1	1,387,530	97,200	7.0
4/1	784,900	51,840	6.6
6/1	538,860	34,560	6.4
Teflon Felt			
2/1	1,568,970	343,440	21.9
4/1	881,668	183,168	20.8
6/1	626,412	122,112	19.5
Teflon Woven			
2/1	1,400,490	174,960	12.5
4/1	791,812	93,312	11.8
6/1	566,508	62,208	11.0

Source: (81)

Ensor et al. present a detailed review of the capital and operating costs of the retrofitted baghouse installation at the Nucla Power Generator Station in their report (46). Three baghouses were retrofitted to three 12,650 Kw spreader stoker boilers in 1973-1974; capital costs associated with these installations are delineated in Table 4-17. Also presented in this table are the approximate 1978 installed system and unit costs which were estimated using the Marshall and Stevens (M&S) cost indices (84). Ensor also reported operating costs which reflected only new or additional expenses incurred by the plant as a result of the baghouse operation. These costs were reported on the basis of 1976 dollars and are presented in Table 4-18.

4.4.2 ESP Costs

Electrostatic precipitators are highly sensitive to fly ash characteristics such as fly ash resistivity. The capital costs are a function of collector area which is in turn a function of parameters such as fly ash loading, fly ash resistivity, and flue gas flowrate. Detailed capital costs for ESP's were developed by the Industrial Gas Cleaning Institute (IGCI) for the EPA (85). These costs were developed for various types of coal, boiler sizes, emission limits, and types of ESP's (hot-side and cold-side). The capital costs IGCI developed for the following cases are presented in Table 4-19:

- Case 1 - a cold-side ESP on a 200 Mw boiler and a .03 $lb/10^6$ Btu emission level,
- Case 2 - a hot-side ESP on a 200 Mw boiler and a .05 $lb/10^6$ Btu emission level,
- Case 3 - a hot-side ESP on a 200 Mw boiler and a .03 $lb/10^6$ Btu emission level, and
- Case 4 - a hot-side ESP on a 700 Mw boiler and a .03 $lb/10^6$ Btu emission level.

In all these cases, the coal composition was the same; consequently, the data in Table 4-19 show the impact of ESP size and location and emission level on capital costs of ESP's on utility boilers. Annualized operating costs for the cases presented in Table 4-19 are given in Table 4-20.

TABLE 4-17. CAPITAL COSTS ASSOCIATED WITH INSTALLATION OF BAGHOUSE AT NUCLA POWER PLANT

Baghouse Equipment and Installation Cost		
Earthwork		$ 39,000
Concrete - foundation		$ 75,000
Structural - stairways, handrails		$ 48,000
Process Equipment		
Baghouse (material only)	$631,000	
Ductwork (material only)	$113,000	
Labor & Other Equipment	$347,000	
Total Process Equipment		$1,091,000
Piping - drainage and air		$ 56,000
Electrical		$ 200,000
Painting		$ 50,000
Instrumentation		$ 50,000
Insulation		$ 130,000
Fly Ash Conveyor System Equipment and Installation Cost		
Earthwork		$ 1,000
Concrete - foundations		$ 10,000
Equipment - controls, valves		$ 130,000
blowers		$ 37,000
Pneumatic conveyor lines		$ 32,000
Electrical		$ 20,000
Painting		$ 5,000
Instruments		$ 10,000
Retrofit Equipment and Installation Cost		
Earthwork		$ 5,000
Demolition - ductwork, concrete		$ 56,000
Modifications		
Ash system		$ 19,000
Rebuild and balance I.D. fans		$ 22,000
Stacks, rebuild tops and relocate		$ 16,000
Condensate and compressed air piping		$ 24,000
Air preheater bypass		$ 30,000
Electrical		$ 20,000
Instruments		$ 6,000
Painting		$ 4,000
Insulation		$ 11,000
TOTAL FIELD COST		$2,220,000
Indirect Owner Cost		
Administration		$ 4,000
Engineering and Supervision		$ 31,000
All Risk Insurance		$ 19,000
Interest During Construction		$ 44,000
Travel, Vehicle, Office, Miscellaneous		$ 22,000
Engineering and Fee		$ 300,000
1973/1974 INSTALLED SYSTEM COST		$2,620,000
APPROXIMATE 1978 INSTALLED SYSTEM COST		$3,590,000
1978 Unit Costs - $100/kw		
- $15/ACFM		
- $41.6/ft^2 of filter		

Source: (46)

TABLE 4-18. ESTIMATED COST OF OPERATING BAGHOUSES AT THE NUCLA POWER PLANT

	$/year	Percent	mills/kwh
Direct Costs			
Operation Labor*	$ (9,500)	(3.3)	(0.05)
Maintenance Labor	2,500	0.9	0.01
Maintenance Material	8,500	3.0	0.05
Utilities	31,000	10.8	0.16
Ash Handling	11,000	3.8	0.06
Subtotal, Directs	$ 53,000	18.5	0.28
Indirect Costs			
Depreciation - 4.9%	127,000	44.3	0.68
Interest - 3.4%	81,000	28.2	0.43
Insurance - 0.1%	3,000	1.0	0.02
Taxes	23,000	8.0	0.12
Subtotal, Indirects	$ 234,000	81.5	1.25
TOTAL	$ 287,000	100.0	1.53

*Not added since no new costs were incurred.

Source: (46)

TABLE 4-19. INVESTMENT COSTS OF ESP'S ON VARIOUS UTILITY BOILERS

CASE:	1	2	3	4
Boiler size, MW	200	200	200	700
Precipitator Type	Cold	Hot	Hot	Hot
Inlet and Outlet Gas Flow				
acfm	798,000	985,000	985,000	3,450,000
$^{\circ}F$	350	700	700	700
acfm	521,000	450,000	450,000	1,580,000
Moisture, Vol. %	10	10	10	10
Particulate Loading				
Inlet gr/acf	1.76	1.43	1.43	1.43
Inlet lb/hr	12,000	12,000	12,000	42,200
Outlet gr/acf	0.009	0.012	0.007	0.007
Outlet lb/hr	60	100	60	210
Removal efficiency, %	99.4	99.2	99.5	99.5
Emission Control Level,				
ng/joule	13	22	13	13
(lb/10^6 Btu)	(0.03)	(0.05)	(0.03)	(0.03)
Equipment Costs				
Device	2,046,100	1,546,100	1,837,000	6,007,300
Auxiliary equipment	207,600	190,200	196,000	609,400
Ash handling equipment	75,600	47,500	52,500	212,700
Total	2,329,300	1,783,800	2,095,500	6,829,400
Installation Costs - Direct				
Foundation and supports	173,000	151,900	166,600	500,500
Insulation	436,600	388,700	424,700	1,372,000
Painting	5,600	5,300	5,600	7,200
Electrical	181,600	133,300	205,300	664,000
Other	1,281,900	949,200	1,144,200	3,574,900
Total	2,078,700	1,628,400	1,946,400	6,119,200
Installation Costs - Indirect				
Engineering	131,200	127,700	129,600	193,100
Construction & field expense	127,700	89,600	107,000	399,900
Construction fees	28,900	27,000	28,000	69,500
Start-up	11,900	11,100	12,300	36,300
Performance tests	25,800	25,800	25,800	56,000
Contingencies	87,800	64,600	76,000	267,100
Total	413,100	345,800	378,700	1,021,900
Total Turnkey Cost	$4,821,100	$3,758,000	$4,420,600	$13,970,500
S/kW Investment (1976)	24.11	18.79	22.10	19.96
(1978)	27.97	21.30	25.64	23.16

Source: (85)

TABLE 4-20. ANNUALIZED OPERATING COSTS OF ESP'S ON VARIOUS UTILITY BOILERS

Case		1	2	3	4
Boiler Size, MW		200	200	200	700
Precipitator Location		Cold	Hot	Cold	Hot
Inlet and Outlet Gas Flow					
acfm		790,000	985,000	985,000	3,450,000
°F		350	700	700	700
acfm		521,000	450,000	450,000	1,380,000
Moisture		10	10	10	10
Particulate Loading					
Inlet gr/acf		2.32	1.43	1.43	1.43
Inlet lb/hr		15,900	12,000	12,000	42,200
Outlet gr/acf		0.009	0.012	0.007	0.007
Outlet lb/hr		60	100	60	210
Removal efficiency, %		99.6	99.2	99.5	99.5
Emission Control Level			13	23	22
ng/joule		13	22	13	13
(lb./10^6 Btu)		(0.03)	(0.05)	(0.03)	(0.03)
Operating Cost Item	unit cost				
Direct Costs					
Operating Labor					
Operator	$10/man-hr	9,130	9,130	10,840	27,280
Supervisor	$12/man-hr	2,520	2,520	2,520	3,780
Total		11,650	13,360	11,650	31,060
Maintenance					
Labor	$10/man-hr	10,980	11,150	11,750	38,840
Materials		3,070	3,590	3,180	12,950
Total		14,050	15,340	14,330	51,790
Replacement Parts		7,500	11,000	9,500	37,000
Utilities					
Electricity	$0.03/kwh	123,330	212,690	168,850	633,730
Total Direct Costs		156,530	253,290	204,330	753,580
Indirect Costs					
Overhead Charges					
Payroll	20% oper. lab.	2,330	2,680	2,330	6,210
Plant	50% lab. & maint.	15,860	14,350	12,990	41,430
Total		15,190	17,030	15,320	47,640
Capitalization Charges	17% of investment	527,950	751,500	638,850	2,374,990
Total Indirect Charges		$543,950	768,530	$654,180	$2,422,630
Total Annualized Cost		$699,670	$1,020,920	$858,510	$3,176,210
Mills/kwh Operating Cost	(1976)	0.40	0.58	0.49	0.52
	(1978)	.46	.62	.57	.60

Basis: 8,760 operating hours per year at 65% capacity factor

Source: (85)

4.4.3 Wet Particulate Scrubber Costs

Although wet particle scrubbers have been widely used in the utility industry, there has been no recent literature reporting detailed capital and operating costs for these devices. However, PEDCo (see Glossary) reported capital and operating costs for several particulate control alternatives including a venturi scrubber (86). Pertinent parameters used to develop the cost of the venturi are presented in Table 4-21. The estimated capital and operating costs associated with achieving two different emission levels with a venturi scrubber are presented in Table 4-22.

4.4.4 Comparative Costs of Particulate Control Devices

Recent cost data are unavailable in many cases and inflation obscures attempts to develop good cost data on the basis of escalation. However, the relative costs of achieving a given emission level with various particulate control devices can be assessed. Stearns-Roger developed an economic comparison between a baghouse and an ESP for a 500 Mw utility boiler; their costs are presented in Table 4-23 (87). The operating costs associated with utilizing a baghouse and various ESP's on a 500 Mw utility boiler are compared in Table 4-24 (87). PEDCo developed capital and operating costs of a cold-side ESP and a venturi scrubber for two emission levels and several sizes of utility boilers; these costs are compared in Table 4-25 (45).

4.5 COMBINING CONTROL PROCESSES TO INCREASE COLLECTION EFFICIENCY

Because of the stringent emission standards that are being established, two or more control processes can be combined in order to reduce the emissions of particulate and gaseous pollutants so that the standards may be met. A recent survey of 43 new or proposed boilers indicates that nearly half of these installations plan or do use a combination of processes for particle and SO_2 control (58). In such instances, it is of interest to project the overall collection efficiency that can be achieved.

The mathematical technique that can be used to predict the overall efficiency attained by a sequence of processes is presented in Table 4-26 and an explanation of this technique follows. The control sequence is assumed to be a dry cyclone separator followed by an electrostatic

TABLE 4-21. VENTURI SCRUBBER DESIGN PARAMETERS

Control System	Design Parameter	Regulation Level, ng/J (lb/10^6 Btu)	
		43 (0.1)	22 (0.05)
Venturi scrubber	L/G ratio, l/m^3 (gal/1000 acf)	2 (15)	2 (15)
	Gas velocity, m/sec (ft/sec)	38 (125)	38 (125)
	Pressure drop, nm H_2O (in. H_2O)	203 (8)	762 (30)

Source: (86)

TABLE 4-22. ESTIMATED COSTS OF A PARTICLE VENTURI SCRUBBER (Mid-$1980)

				Particulate Control Alternative		
				Venturi Scrubbers		
	Coal				Annual Cost (mills/kwh)	
Regulation Level	Sulfur (%)	Ash (%)	Boiler Capacity (megawatts)	Capital Cost ($/kW)	O&M	Fixed
22.0 ng/j (.05 lb/10^6 BTU)						
	3.5	14.0	25	178.48	1.45	7.15
			100	128.10	1.30	5.15
			500	72.63	0.80	3.03
			1000	68.65	0.78	2.87
43.0 ng/j (.1 lb/10^6 BTU)						
	3.5	14.0	25	112.52	1.42	4.51
			100	99.97	1.26	4.02
			500	58.67	0.77	2.45
			1000	57.21	0.75	2.39

Source: (91)

TABLE 4-23. CAPITAL COST COMPARISON FOR BAGHOUSE AND ESP'S FOR A 500 MW UTILITY BOILER

Coal	Collector Type	Limit (lb/10^6 BTU)	Minimum Efficiency %	SCA or A/C Ratio (ACFM/ft^2)	Gas Flow, 10^6 acfm	Collection Area (60^3 ft^2)	No. Modules Value	No. Modules Factor	Capital Investment (\$$10^6$, 1977)
Wyoming	Hot-Side ESP	0.10	99.18	368	2.68	985	--	--	23.2
		0.05	99.64	462	2.68	1239	--	--	26.3
		0.014	99.50	683	2.68	1830	--	--	33.0
	European Cold-Side ESP	0.10	99.28	536	1.86	996	--	--	19.3
		0.05	99.64	704	1.86	1309	--	--	24.0
		0.014	99.60	1155	1.86	2148	--	--	35.6
	Fabric Filter*	--		1.93	1.86	964	20	1.06	14.3
		--		1.93	1.86		20	1.06	14.3
		--		1.93	1.86		40	1.25	16.9
North Dakota Lignite	American Cold-Side ESP	0.10	99.34	326	2.41	785	--	--	17.1
		0.05	99.67	410	2.41	987	--	--	19.6
		0.014	99.91	588	2.41	1418	--	--	24.4
	Fabric Filter	--		1.93	2.41	1332	20	1.05	17.2
Alabama	Hot-Side ESP	0.10	98.85	263	2.43	645	--	--	17.2
		0.05	99.32	336	2.43	824	--	--	19.8
		0.014	99.81	515	2.43	1263	--	--	25.6
	American Cold-Side ESP	0.10	98.65	473	1.97	928	--	--	16.1
		0.05	99.32	336	2.43	824	--	--	19.6
		0.014	99.81	1050	1.97	2063	--	--	26.0
	European Cold-Side ESP	0.10	98.65	420	1.97	825	--	--	17.3
		0.05	99.32	630	1.97	1238	--	--	19.2
		0.014	99.81	1050	1.97	2063	--	--	26.0
	Fabric Filter	--		1.93	1.97	1086	20	1.06	14.9
Eastern High Sulfur	American Cold-Side ESP	0.10	99.48	441	2.0	917	--	--	16.4
		0.05	99.74	567	2.10	1191	--	--	19.1
		0.014	99.93	830	2.10	1743	--	--	24.0
	Fabric Filter	--		1.93	2.10	1161	20	1.06	15.6

* Three figures shown for the fabric filter applied to Wyoming coal are, from top to bottom, for a 20-compartment system and 2-year bag-replacement cycle, a 20-compartment system and 4-year bag-replacement, and a 40-compartment system and 2-year bag-replacement, respectively.

Source: (87)

TABLE 4-24. COMPARISON OF ANNUAL OPERATION AND MAINTENANCE COSTS FOR BAGHOUSE AND ESP'S FOR A 500 MW UTILITY BOILER

				Collection System			Ash-Removal System			
Coal	Collector	Emission Limit (lb/10^6 BTU)	Collection Area (10 ft^6)	Operation ($/yr)	Maintenance ($/yr) Material	Maintenance ($/yr) Labor	Operation ($/yr)	Maintenance ($/yr) Material	Maintenance ($/yr) Labor	Total Operation tion & Maintenance ($/yr, 1977)
Wyoming	Hot-Side ESP	0.10	0.985	20,000	25,000	25,000	60,000	30,000	40,000	190,000
		0.05	1.239	20,000	31,000	31,000	60,000	37,000	37,000	216,000
		0.014	1.830	20,000	45,000	45,000	60,000	55,000	55,000	380,000
	European Cold-Side EPS	0.10	0.996	20,000	15,000	15,000	60,000	10,000	10,000	130,000
		0.05	1.309	20,000	20,000	20,000	60,000	13,000	13,000	146,000
		0.014	2.148	20,000	32,000	32,000	60,000	21,000	21,000	186,000
	Fabric* Filter	—	0.964	20,000	270,000	34,000	60,000	7,700	7,700	400,000
				20,000	135,000	17,000	60,000	7,700	7,700	248,000
				20,000	270,000	34,000	60,000	14,000	14,000	412,000
North Dakota Lignite	American Cold-Side ESP	0.10	0.785	20,000	20,000	20,000	60,000	7,900	7,900	136,000
		0.05	0.987	20,000	25,000	25,000	60,000	10,000	10,000	150,000
		0.014	1.418	20,000	35,000	35,000	60,000	14,000	14,000	178,000
	Fabric Filter	—	1.249	20,000	350,000	44,000	60,000	10,000	10,000	493,000
	Hot-Side ESP	0.10	0.645	20,000	16,000	16,000	60,000	19,000	19,000	150,000
		0.05	0.824	20,000	21,000	21,000	60,000	25,000	25,000	172,000
		0.014	1.263	20,000	32,000	32,000	60,000	38,000	38,000	220,000
	American Cold-Side ESP	0.10	0.928	20,000	32,000	32,000	60,000	9,000	9,000	162,000
		0.05	1.238	20,000	43,000	43,000	60,000	12,000	12,000	190,000
		0.014	2.063	20,000	72,000	72,000	60,000	21,000	21,000	266,000
Alabama										
	European Cold-Side ESP	0.10	0.825	20,000	12,000	12,000	60,000	8,300	8,300	121,000
		0.05	1.094	20,000	16,000	16,000	60,000	11,000	11,000	134,000
		0.014	1.816	20,000	27,000	27,000	60,000	18,000	18,000	170,000
	Fabric Filter	—	1.021	20,000	286,000	36,000	60,000	8,200	8,200	419,000
	American Cold-Side	0.10	0.927	20,000	32,000	32,000	60,000	9,300	9,300	162,000
		0.05	1.191	20,000	42,000	42,000	60,000	12,000	12,000	188,000
Eastern High-Sulfur	ESP	0.014	1.743	20,000	61,000	61,000	60,000	17,000	17,000	230,000
	Fabric Filter	—	1.088	20,000	305,000	38,000	60,000	8,700	8,700	440,000

* Entries for Wyoming coal applied to the fabric filter represent three alternatives — from to to bottom, the 20-compartment system with a 2-year bag-replacement cycle, the 20-compartment system with a 4-year bag-replacement cycle, and the 40-compartment system with a 2-year bag-replacement cycle.

Source: (87)

TABLE 4-25. CAPITAL COST COMPARISON OF AN ESP AND A VENTURI SCRUBBER

				PARTICULATE CONTROL ALTERNATIVE								
	Coal			Fabric Filters[a]			Electrostatic Precipitators			Venturi Scrubbers[b]		
Regulation Level	Sulfur (%)	Ash (%)	Boiler Capacity (megawatts)	Capital Cost ($/kW)	Annual Cost (mills/kWh) O&M	Annual Cost (mills/kWh) Fixed	Capital Cost ($/kW)	Annual Cost (mills/kWh) O&M	Annual Cost (mills/kWh) Fixed	Capital Cost ($/kW)	Annual Cost (mills/kWh) O&M	Annual Cost (mills/kWh) Fixed
22.0 ng/J	3.5	14.0	25				89.90	1.81	2.68	178.48	1.45	7.15
			100				53.16	0.91	1.59	128.10	1.30	5.15
			500				28.21	0.47	0.84	72.63	0.80	3.03
			1000				24.76	0.41	0.74	68.65	0.78	2.87
43.0 ng/J	3.5	14.0	25				91.80	1.82	2.74	112.52	1.42	4.51
			100				51.11	0.87	1.53	99.97	1.26	4.02
			500				26.85	0.45	0.80	58.67	0.77	2.45
			1000				23.61	0.39	0.71	57.21	0.75	2.39

[a] Level examined was 13.4 ng/J.

[b] Costs are for venturis as an integral part of a flue gas desulfurization system.

Source: (45)

TABLE 4-26. PREDICTED OVERALL COLLECTION EFFICIENCY FOR A CYCLONE AND ESP COMBINATION

Particle Size Distribution, Microns	Particle Size Midpoint of Range, Microns	Fraction of Total Dust in Range, %		Cyclone Efficiency at Midpoint, %*		Dust Collected in Cyclone, %	Fraction of Dust from Cyclone in Range		Electrostatic Precipitator Efficiency at Midpoint, %		Dust Collected in ESP, %
0-2.5	1.25	12	x	33.5	=	4.0	50.3	x	77.0	=	38.7
2.5-5	3.75	8	x	64.5	=	5.2	17.6	x	90.5	=	16.0
5-7.5	6.25	6	x	76.7	=	4.6	8.8	x	94.0	=	8.3
7.5-10	8.75	4	x	84.2	=	3.4	3.8	x	95.0	=	3.6
10-15	12.50	8	x	89.3	=	7.1	5.7	x	95.5	=	5.4
15-20	17.50	7	x	92.0	=	6.4	3.8	x	96.0	=	3.7
20-30	25	10	x	94.3	=	9.4	3.8	x	96.5	=	3.7
30-40	35	10	x	96.0	=	9.6	2.5	x	96.8	=	2.4
40-60	50	15	x	97.3	=	14.6	2.5	x	97.7	=	2.4
60-75	67.50	10	x	98.5	=	9.9	0.6	x	98.7	=	0.6
75-104	89.50	7	x	99.1	=	6.9	0.6	x	99.2	=	0.6
104-150	127	3	x	100.0	=	3.0	--		--		--
						84.1%					85.4%

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*Efficiencies assumed.

Calculating emitted dust from collected:

Percent of 1.25 micron dust emitted $= \frac{12 - 4.0}{100 - 84.1} = 50.3\%$

Calculating combined efficiency:

Cyclone fraction emitted = 1,000 - 0.841 = 0.159

Precipitator fraction emitted = 1.000 - 0.854 = 0.146

Combined fraction emitted = 0.159 x 0.146 = 0.0232

Combined fraction collected = 1 - 0.0232 = 0.977

Combined percent collected = 97.7%

precipitator. Knowing the size distribution of fly ash discharged from the boiler and the cyclone's collection efficiencies for the various particle size ranges allows the percentage removal of particles in a given size range to be calculated. The summation of the respective collection efficiencies yields the total collection efficiency exhibited by the cyclone. Since the cyclone removes the different sized particles to varying degrees, the fly ash exiting the cyclone exhibits a new size distribution. The fraction each particle size makes up of the distribution can be calculated by the following expression:

$$\%\text{ of total distribution for given particle size} = \frac{A - B}{100 - C} \qquad (4\text{-}1)$$

where:

A = fraction of fly ash leaving boiler (%),
B = fraction of fly ash exiting control process (%), and
C = overall collection efficiency of control process (%).

For a 1.25 μm particle, the fraction of the fly ash exiting the cyclone is 50.3 percent. By multiplying the fraction of each size range that makes up the total fly ash exiting the cyclone by the collection efficiency exhibited by the ESP for each size range, the fraction of dust collected in each range is calculated. As before, summation of these collection efficiencies yields the ESP's overall collection efficiency. Once the overall efficiency of each process is known, the efficiency of the combination is calculated as follows:

Cyclone fraction emitted = 1.00 - 0.841 = 0.59
Precipitator fraction emitted = 1.00 - 0.854 = 0.146
Combined fraction emitted = .159 x .146 = .0232
Combined fraction collected = 1.0 - .0232 = .977
Combined percent collected = 97.7%

The overall collection efficiency that is achieved by a combination of control processes for a specific trace element can be approximated by an approach that is similar to the one presented in Table 4-26; however, additional data that correlate trace element concentration and particle size are required. These data may be expressed in units of concentration or enrichment. Enrichment is defined as the fractional distribution for an element in a stream relative to the fractional distribution for ash in that stream. For example, assume 1.6 percent of the ash is emitted as fly ash. If no enrichment (increase in concentration) occurs for the trace metal being considered, then 1.6 percent of that metal is emitted in the fly ash. If, however, 1.85 percent of that metal is emitted, then its subsequent enrichment is about 1.85/1.6 or about 1.15. If an enrichment factor of less than one occurs then the specie has been depleted. In order to illustrate how the overall trace element collection efficiency of a treating sequence could be approximated, it is assumed that the sequence will consist of an electrostatic precipitator followed by a venturi scrubber. The electrostatic precipitator is assumed to have an overall collection efficiency of 85 percent for copper. Calculation of the venturi's collection efficiency is shown in Table 4-27 (63).

4.6 EMERGING CONTROL TECHNIQUES

The utility industry is currently investigating various ways to reduce trace element emissions. One technique involves washing the coal with a solvent before it is combusted; however, no information on the effectiveness of this technique is available (88-90). Experiments conducted with a bench-scale, fluidized-bed combustion have shown that fluidized combustion offers significant potential for reducing trace element emissions (91, 92).

Several processes are currently being developed to achieve further removal of fine particles and, correspondingly, trace elements. These processes are in various stages of development ranging from conceptual design to full-scale operating units. Those processes that appear to be the most promising at this time are briefly discussed below.

4.6.1 Steam-Hydro Air Cleaning System

This system has recently been developed by Lone Star Steel and utilizes a high-speed steam drive with injected water to remove particles. Normally, the system operates on energy produced by waste heat captured from the process being controlled. The heat is used to generate steam in a

TABLE 4-27. APPROXIMATION OF VENTURI SCRUBBER'S COPPER COLLECTION EFFICIENCY

Characteristics of Ash Exiting the ESP									
Particle[1] Size (µm)	Ash Fraction[1] Distribution(%)		Enrichment[1]		Concentration A[2]		Venturi[3] Removal Efficiency (%)		Concentration B[4]
>8.0	9.5	x	1.4	=	13.30	x	100	=	13.30
5.0-8.0	11.4	x	1.8	=	20.52	x	99.5	=	20.42
3.3-5.0	16.6	x	1.5	=	24.90	x	99.15	=	24.69
2.3-3.3	11.6	x	1.7	=	19.72	x	99	=	19.52
1.5-2.3	20.9	x	2.0	=	41.80	x	99	=	41.38
.74-1.5	17.2	x	2.4	=	41.28	x	96.86	=	39.98
.45-.74	8.6	x	2.6	=	22.36	x	91.5	=	20.46
.30-.45	2.7	x	2.7	=	7.29	x	78	=	5.69
<.30	1.6	x	9.7	=	15.52	x	70	=	10.86
					ΣA = 206.69				ΣB = 196.57

Overall venturi collection efficiency for copper $= \frac{B}{A} \times 100$

$= 95\%$

Overall collection efficiency of sequence:

ESP = 1 - .85 = .15

Venturi = 1 - .95 = .05

Fraction emitted = .15 x .05 = .075

Combined fraction collected = 1 - .075 = .9925

Combined collection efficiency = 99.25%

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[1] Ash characteristics from (63)

[2] Concentration A = Concentration of copper on given particle size exiting if no further control used.

[3] Typical venturi particle size collection efficiencies from (40).

[4] Concentration B = Concentration of copper removed in each size range.

waste heat boiler. Steam requirements are reported to be 0.002-0.01 lb/ft^3 of gas, while required water rates are approximately 230 lb/1000 ft^3 of gas.

Preliminary tests indicate that 99.5 percent collection efficiency could be obtained for a dust having a mass mean diameter of 1.5 microns at an average loading of 1.26 grains/scf. Based on the results of preliminary tests, the Steam-Hydro system offers excellent promise as a new system for the control of fine particle emissions (41, 93).

4.6.2 ADTEC Wet Scrubber

The ADTEC system, developed by Aronetics, Inc., Tullahoma, Tennessee, is a wet scrubbing system that operates on the conventional venturi collection mechanisms of inertial impaction, but establishes the required particle-droplet differential velocity by utilizing waste process heat rather than external energy. Water (at 300 psi) is heated to 150-205°C by the flue gas and is then atomized by partial flashing and expansion through a nozzle. Dirty gas is introduced into the two-phase mixture of steam and water; cleaning occurs primarily by impaction. The water and collected dust are separated from the gas, while the remaining steam exits with the flue gas.

A test unit was installed on a ferro-alloy furnace of the Chromium Mining and Smelting Corporation (Chromasco) at Woodstock, Tennessee. Collection efficiencies of 99+ percent were reported. Mechanical energy consumed in pumping the water to the required pressure of 275-300 psi is about 3 hp/1000 cfm of gas while the power required in the form of heat input to the water from the gas stream exceeds 200 hp/1000 cfm. Capital costs have been established by Aronetics to be between those of venturi scrubbers and fabric filters.

On the basis of currently available information, this system also appears to offer significant improvement in the collection of fine particles at modest energy consumption rates where a waste gas which contains a sufficient amount of thermal energy to heat the water is available (41).

4.6.3 Wetted-Knit Mesh Filters

Scrubbing systems in which a wetted-knit mesh filter is utilized have recently been developed and promoted by Heat-Systems-Ultrasonics and by Dupont. In both systems the gas stream is first sprayed with water and then the gas-liquid mixture is passed through a fiber bed structure having a pore size and pore length that are sufficiently fine and long enough to provide intimate contact of the gas stream containing the particulate solids and mist with the scrubber liquid. In performance tests conducted by Dupont with a laboratory-scale unit, the wetted-knit mesh filter exhibited a collection efficiency of greater than 80 percent for a dust having a size distribution of 50 percent <2.4 μm, 28 percent <1 μm, and 14 percent <0.5 μm. If the efficiencies reported by Dupont for their laboratory-scale system can be substantiated by testing of pilot-scale or demonstration-scale systems, wetted-knit mesh filters will be an addition to technology for the control of fine particulates (41).

4.6.4 Other Technologies

Other control processes that may be effective for removing fine particulates include Cross-Flow Nucleation Scrubber, Pentapure Impinger, Dynactor Wet Scrubber, Mystaire Scrubber, Dupont Wet Scrubber, granular bed filters, fluidized beds, condensation scrubbers, foam scrubbers, charged droplet scrubbers, electrified filters, gamma-ray precipitator, and sonic agglomerators. Descriptions of these processes are presented in Evaluation of Eight Novel Fine Particle Collection Devices (92).

4.7 UNAVAILABLE DATA

Further data are needed before a comprehensive assessment of fine particulate and trace element emissions from coal combustion technologies can be conducted. These data include the following:

- More information characterizing particulate and trace element emissions from various coal using technologies is needed.
- More information characterizing the abilities of the various control processes being used in the utility industry

to reduce trace element emissions at various dust loadings is needed.

- More data regarding the trace element collection efficiencies of a baghouse applied to a conventional combustion source are needed.
- Current cost data for different control processes are needed.
- Operating data showing the overall trace element collection efficiency achieved by a combination of control processes are needed.

Presently, electrostatic precipitators and baghouses exhibit the highest trace element removal efficiencies of all the commercially proven control processes. Optimization studies focused on increasing the efficiencies and reliabilities of these processes should be conducted. An ESP optimization study might consider the effect of conditioning ash with a chemical additive on trace element collection efficiency. For baghouses, various filter fabrics should be tested in order to find fabrics that are more resistant to thermal and chemical degradation.

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SECTION 5

TRACE ELEMENT EMISSIONS FROM SCCP

The law of conservation of matter requires that trace elements that enter a combustion process must leave the process and return to the environment. Combustion processes change the matrices in which trace elements occur. They also change the physical location of trace elements in the environment. In addition, combustion processes may change chemical forms, concentrations and physical states of trace elements. These changes can be expected to influence the effects that trace elements have on the environment and on the human population.

This section reports information taken from the literature concerning the amounts of trace elements leaving combustion processes. These trace element emissions can be reported in several ways. The three most common ways to report trace element emissions are: as a function of time, as a function of volume of the effluent stream, and as a function of the heating value of the fuel. All three ways of reporting effluents occur in this section.

Trace elements from combustion processes are directly emitted to the air, to the land and to surface waters. Emissions to the air may be as suspended particles or as vapors. Emissions to the land are as solid wastes (ashes and flue gas desulfurization sludges). Direct emissions to surface waters come from cleaning operations, from discharge of spent cooling water, and from flue gas desulfurization processes.

Secondary or indirect emission of trace elements to the environment occurs when natural waters interact with solid waste. Rain water, surface water or ground water will leach trace elements from solid waste and then the leachate can enter the environment.

The bulk of the information available in the literature concerns trace element emissions from coal-fired utility boilers. This distribution of information reflects the fact that coal combustion has a higher potential than other combustion processes for discharge of trace elements to the environment. The amount of coal burned, the amount of ash produced, and the trace element concentrations in the ash combine to make coal combustion the major potential source of trace element emissions to the environment.

Coal, however, accounts for only about twenty seven percent of domestic (non-transportation) fossil fuel consumption. Oil, usually less than 0.1 percent ash accounts for thirty five percent of fossil fuel comsumption (natural gas is thirty-eight percent), and, therefore, cannot be neglected as a potential source of trace metal pollutants.

Most trace elements in fuels remain in the ash after combustion. These trace elements are more concentrated in the ash then they were in the fuel. Coal combustion produces much more ash than does combustion of oil. Although combustion of coal and wood produce comparable amounts of ash, significantly more coal is used as fuel. The emphasis on utility boilers reflects the fact that more coal is burned in utility boilers than in other combustion facilities.

Information relating to emissions from coal-fired facilities is presented in the first five sections of this chapter. Studies of trace element emissions to the atmosphere from coal-fired facilities are discussed first. Atmospheric emissions which could be related to the heating value of the coal are discussed in Section 5.1. Atmospheric emissions which could not be related to the heating value of the coal are discussed in Section 5.2.

Trace element emissions associated with solid waste and aqueous effluents are presented next. Solid wastes and primary aqueous effluents are discussed in Section 5.3 and secondary aqueous effluents are discussed in Section 5.4

Observed distributions of trace elements in various ash streams within a coal combustion facility are presented in Section 5.5. This section includes data relating to enrichment of some trace elements in various size fractions of fly ash. Data demonstrating surface predominance of some elements on the surfaces of fly ash particles is presented.

The next sections present available information concerning emissions from the combustion of oil and gas, municipal refuse, and wood. Identification of data gaps and suggestions for further work complete this chapter.

5.1 TRACE ELEMENT EMISSIONS TO THE ATMOSPHERE FROM COAL-FIRED POWER PLANTS IN TERMS OF HEATING VALUE OF COAL

Many studies of atmospheric emissions from coal-fired power plants have been reported. Reports from five of these studies included the heating value of coal and enough other information so that emissions could be calculated as weight of element released per unit heating value of the coal. The data from these studies have been recalculated in these terms. The results of these calculations are listed in Tables 5-1 and 5-2.

Emission values are listed for twelve sets of measurements. These data represent measurements on ten coal-fired boilers at seven plants. The reports that the data were taken from are Ondov et al. (1), Lyon (2), Mann et al. (3), Radian (4) and Cowherd et al. (5). Several analytical techniques were employed and the reliability of the data varies from study to study and often even for individual elements within a given study.

The units chosen for reporting trace element emissions are grams of the element per trillion (10^{12}) joules of energy in the coal. The amount of electricity which can be generated from 10^{12} joules will vary somewhat with the efficiency of the plant, but typically, about 140 megawatt-hours of electricity can be produced. The numbers in the table then represent the hourly emission rate of a 140 MW plant operating at capacity. Multiplication of the numbers by 7 will give the approximate hourly emission of a 1000 MW plant operating at capacity.

The tables are arranged according to the type of particle control device employed on the units studied. Electrostatic precipitators are the most common type of unit used to control particulate emissions from coal-fired boilers. Cold-side electrostatic precipitators are located on the downstream side (cold side) of the air preheater. Hot-side electrostatic precipitators are located on the upstream side of the air preheater. See

TABLE 5-1. ATMOSPHERIC EMISSIONS OF TRACE ELEMENTS FROM COAL-FIRED POWER PLANTS WITH COLD-SIDE (CS) OR HOT-SIDE (HS) ELECTROSTATIC PRECIPITATORS FOR PARTICULATE CONTROL

(Grams Element Emitted Per 10^{12} Joules in the Coal)*

		Particulate Control with Cold-Side Electrostatic Precipitators				Particulate Control with Hot-Side Electrostatic Precipitators	
	Plant Designation	Unit 3	Allen	Allen	CS Unit 1	Station II	HS Unit 2
	Firing Method	PC	CYC	CYC	PC	PC	PC
	Coal Type	Western	Eastern	Eastern	Western	Western	Western
	First Author	Ondov	Lyon	Lyon	Mann	Radian	Mann
Element	Date	July 1975	Jan 1972	Aug 1973	Sept 1976	Oct 1974	Sept 1976
Aluminum		15,600.	13,000.	800.		3200.	
Antimony		2.15		5.		0.3	
Arsenic		15.3	6.	5.	1.1	0.08	4.6
Barium		807.	16.	8.		< 26.	
Beryllium		0.72			0.17	0.43	0.40
Bismuth						0.08	
Boron						94.	
Bromine		6.6	0.6			0.4	
Cadmium		0.26	0.3	0.6	0.18	< 0.2	0.77
Calcium		3400.	600.	300.		5700.	
Cerium		16.		1.		0.8	
Cesium		0.410	0.3	0.3		< 0.08	
Chlorine				2.		3000.	
Chromium		9.58	20.	8.	4.0	60.	13.
Cobalt		2.38	1.	0.5		1.5	
Copper			20.	2.	37.	2.8	23.
Dysprosium		1.12				< 0.08	
Erbium						< 0.08	
Europium		0.164		0.01		< 0.08	
Fluorine					691.	280.	330.
Gadolinium						< 0.08	
Gallium		18.7				3.4	
Germanium						0.2	
Gold						< 0.08	
Hafnium		1.37		0.05		< 0.08	
Holmium						< 0.08	
Indium		0.138				-	
Iodine						< 0.08	
Iridium						< 0.08	
Iron		3670.	6000.	2000.		980.	
Lanthanum		8.96	1.	0.5		0.6	
Lead			6.	5.		6.2	
Lithium						0.2	
Lutetium		0.164				< 0.08	
Magnesium		1360.	2000.			830.	
Manganese		41.2	26.	5.	8.7	19.	16.
Mercury				3.(gas)	0.92	1.7	0.77
Molybdenum		6.48				3.2	

(Continued)

* These numbers represent the hourly emission rate of each element from a plant with approximately 140 MW capacity.

SOURCE: Ondov et al. (1); Lyon (2); Mann et al. (3) and Radian (4).

TABLE 5-1. (Cont'd)

(Grams Element Emitted Per 10^{12} Joules in the Coal)*

		Particulate Control with Cold-Side Electrostatic Precipitators				Particulate Control with Hot-Side Electrostatic Precipitators	
	Plant Designation	Unit 3	Allen	Allen	CS Unit 1	Station II	HS Unit 2
	Firing Method	PC	CYC	CYC	PC	PC	PC
	Coal Type	Western	Eastern	Eastern	Western	Western	Western
		Ondov	Lyon	Lyon	Mann	Radian	Mann
Element	Date	July 1975	Jan 1972	Aug 1973	Sept 1976	Oct 1974	Sept 1976
Neodymium		6.05				1.1	
Nickel				2.	2.5	30.	9.8
Niobium						0.4	
Osmium						< 0.08	
Palladium						< 0.08	
Phosphorous						450.	
Platinum						< 0.08	
Potassium		905.	600.	200.		77.	
Praseodymium						0.2	
Rhenium						< 0.08	
Rhodium						< 0.08	
Rubidium		5.52	-	2.		0.6	
Ruthenium						< 0.08	
Samarium		1.14	-	0.08		< 0.08	
Scandium		1.96	5.	0.3		0.4	
Selenium		5.82	32.	10**, 0.8	0.59	13.	7.7
Silver						0.04	
Sodium		2210.	300.	100.		190.	
Strontium		85.4				170.	
Sulfur						245,000.	
Tantalum		0.323		0.02		< 0.08	
Tellurium						0.2	
Terbium		0.112				< 0.08	
Thallium						< 0.08	
Thorium		3.67		0.6		< 0.08	
Thulium						< 0.08	
Tin						0.6	
Titanium		892.		100.	94.	230.	635.
Tungsten		2.78				< 0.08	
Uranium		3.29	1.	0.8	0.28	0.32	0.79
Vanadium		39.7	30.	10.		26.	
Ytterbium		0.503				< 0.08	
Yttrium						8.5	
Zinc		44.8	60.	50.	46.	8.7	14.
Zirconium		34.6				3.4	
TSP		123,000.					

* These numbers represent the hourly emission rate of each element from a plant with approximately 140 MW capacity.

**Selenium was analyzed by two methods. Gas chromatography-Microwave emission spectroscopy gave a value of 10 grams selenium per 10^{12} joules. Neutron activation analysis gave a value of 0.8.

SOURCES: Ondov et al., (1); Lyon, (2); Mann et al., (3); and Radian, (4).

TABLE 5-2. ATMOSPHERIC EMISSIONS OF TRACE ELEMENTS FROM COAL-FIRED POWER PLANTS WITH WET SCRUBBERS OR CYCLONES FOR PARTICULATE CONTROL

(Grams Element Emitted Per 10^{12} Joules in Coal)*

		Particulate Control with Wet Scrubbers				Particulate Control with Cyclones	
	Plant Designation	Unit 1	Unit 1	Unit 2	Station I	Station III	Widow's Creek
	Firing Method	PC	PC	PC	PC	CYC	PC
	Coal Type	Western	Western	Western	Western	Western	Eastern
	First Author	Ondov	Ondov	Ondov	Radian	Radian	Cowherd
Element	Date	June 1975	Feb 1976	June 1975	Sept 1974	Aug 1974	Mid 1974
Aluminum		1320.	680.	1130.	3610.	72,700.	
Antimony		3.26	1.38	1.7	0.37	19	2.30
Arsenic		13.5	5.24	9.2	4.6	120.	13.7
Barium		450.	97.9	580.	90.	< 680.	1600.
Beryllium					0.26	3.	14.1
Bismuth					0.2	3.6	
Boron					146.	6600.	
Bromine		2.0	0.98	0.53	< 0.2	8.0	
Cadmium				0.84	1.7	6.8	13.0
Calcium			782.		12,000.	178,000.	31,000.
Cerium		0.93	0.48	0.45	2.8	27.	
Cesium			0.014		3.7	27.	
Chlorine		63.	37.0	49.	3900.	4300.	916.
Chromium		20.7	13.4	3.4	170.	430.	331.
Cobalt		0.57	0.165	0.30	2.8	30.	5.7
Copper			11.6	8.8	13.	210.	112.
Dysprosium		.055	0.026	0.051	< 0.2	2.3	
Erbium					< 0.2	0.8	
Europium		0.012	0.0074	0.012	< 0.2	1.5	
Fluorine					190.	3700.	1020.
Gadolinium					0.4	3.	
Gallium		5.3	2.01	2.9	12.	410.	
Germanium					1.3	140.	
Gold					< 0.2	< 1.4	
Hafnium		0.075	0.032	0.050	< 0.2	< 1.4	
Holmium					< 0.2	< 1.4	
Indium		0.019	0.0140	0.014			
Iodine		1.21		0.82	< 0.2	< 1.4	
Iridium					< 0.2	< 1.4	
Iron		455.	239.	425.	2000.	31,000.	169,000.
Lanthanum		0.46	0.275	0.45	2.6	10.	
Lead					11.	37.	57.
Lithium					1.5	14.	
Lutetium		.0052	0.0045	0.010	< 0.2	< 1.4	
Magnesium		230.	112.	290.	2000.	44,000.	
Manganese		38.	23.0	15.7	48.	710.	313.
Mercury					4.8	10.	27.
Molybdenum		4.3	2.07	2.7	79.	340.	

(Continued)

* These numbers represent the hourly emission rate of each element from a plant with approximately 140 MW capacity.

SOURCE: Ondov *et al*. (1); Radian, (4): Cowherd *et al*., (5).

TABLE 5-2. (Cont'd)

		(Grams Element Emitted Per 10^{12} Joules in Coal)*					
		Particulate Control with Wet Scrubbers				Particulate Control with Cyclones	
	Plant Designation	Unit 1	Unit 1	Unit 2	Station I	Station III	Widow's Creek
	Firing Method	PC	PC	PC	PC	CYC	PC
	Coal Type	Western	Western	Western	Western	Western	Eastern
	First Author	Ondov	Ondov	Ondov	Radian	Radian	Cowherd
Element	Date	June 1975	Feb 1976	June 1975	Sept 1974	Aug 1974	Mid 1974
Neodymium		0.27	0.32	0.55	3.5	10.	
Nickel		15.	13.3		22.	319.	190.
Niobium					2.8	10.	
Osmium					< 0.2	< 1.4	
Palladium					< 0.2	< 1.4	
Phosphorous					830.	-	
Platinum					< 0.2	< 1.4	
Potassium		41.	27.7	49.	400.	22,000.	
Praseodymium					0.4	2.9	
Rhenium					< 0.2	< 1.4	
Rhodium					< 0.2	< 1.4	
Rubidium					11.	370.	
Ruthenium					< 0.2	< 1.4	
Samarium		0.061	0.0355	0.055	< 0.2	< 1.4	
Scandium		0.127	0.0552	0.097	< 0.2	< 1.4	
Selenium		20.5	12.9	21.0	3.7	35.	< 26.
Silver					1.5	<0.4	
Sodium		230.	170.	219.	3100.	41,000.	
Strontium		18.4	9.44	20.	181.	5100.	
Sulfur					259,000.	871,000.	
Tantalum		0.056	0.017	0.022	0.4	3.5	
Tellurium					0.2	7.4	< 49.
Terbium					< 0.2	< 1.4	
Thallium					1.3	22.	
Thorium		0.22	0.102	0.195	0.2	< 1.4	
Thulium					< 0.2	< 1.4	
Tin					12.	670.	2.8
Titanium		76.	43.1	77.	170.	2000.	10,300.
Tungsten		2.26	1.04	2.72	0.9	11.	
Uranium		1.08	0.527	0.58	1.2	15.	
Vanadium		16.6	9.39	19.9	200.	290.	652.
Ytterbium		0.021	0.0187	0.0136	< 0.2	< 1.4	
Yttrium					1.3		
Zinc		8.8	5.83	4.6	120.	350.	596.
Zirconium			2.46	6.6	2.6	73.	
TSP			10,900.				

* These numbers represent the hourly emission rate of each element from a plant with approximately 140 MW capacity.

SOURCES: Ondov _et al_. (1); Radian, (4); Cowherd _et al_., (5).

Section 4 of this report for a more complete definition of types of electrostatic precipitators. Table 5-1 lists emissions reported from three units with cold-side electrostatic precipitators and two units with hot-side electrostatic precipitators. One of the units with cold-side precipitators was sampled in 1972 and again in 1973. Although the plants are not identified, striking similarities between the plant descriptions for the units with hot-side electrostatic precipitators lead one to believe that the units sampled are located at the same generating station. Unit One was sampled for one study and Unit Two was sampled for the other study. Atmospheric emissions of most elements vary widely even for the three cold-side electrostatic precipitators. Some of this variation can be ascribed to differences in precipitator efficiency. Other differences are probably related to differences in trace element concentrations in the coal, differences in concentrations of major elements in the coal ash, different types of boilers and possibly other variables. Failure to collect representative samples and analytical errors also contribute to observed differences. The same factors influence differences between emissions from hot-side electrostatic precipitators and cold-side electrostatic precipitators. In addition, the different temperature history of the collected particles influences the emission rates of some elements. Emission rates of elements which volatilize and then condense are most likely to be influenced by temperature variations.

Table 5-2 lists atmospheric emission rates as a function of heating value of the coal for coal-fired boilers with other types of particles control devices. The particle control devices on the units were wet scrubbers and cyclones (mechanical collectors). The emission rates from the scrubbers studied generally varied less than those from other types of control devices. All plants listed with scrubbers for particle control fired pulverized western coal.

Emissions from units using cyclones for particle control generally were higher than emissions from units with other particle control devices. This reflects the generally lower efficiencies of cyclones. Differences in calcium, iron and other elemental emissions from the two plants with cyclone collectors reflect the different concentrations of many elements in eastern and western coal ashes.

The studies which provided the data listed in Tables 5-1 and 5-2 are described briefly in the following sections. Plant descriptions and key operating parameters are given.

5.1.1 Studies of Trace Element Emissions from a Western Power Plant; Comparison of a Venturi Wet Scrubber System with a Cold-Side Electrostatic Precipitator

Ondov et al. (1) reported trace element emissions to the atmosphere for three units of the same western power plant. Particles were controlled by a venturi wet scrubber on two units. Particles were controlled with an electrostatic precipitator on the third unit. Samples of particulates leaving the control device were collected from one or more of these units during three time periods. The first set of samples was tkaen in June 1975, the second set was collected in July 1975, and the third set was taken in February 1976.

Table 5-3 lists the characteristics of the units sampled. Only particulate matter was collected. Trace elements present in the flue gas in the vapor phase were not collected. Trace elements were measured using instrumental neutron activation analysis (INAA), atomic absorption spectrophotometry, and X-ray fluorescence.

TABLE 5-3. CHARACTERISTICS OF UNITS AT WESTERN POWER PLANT STUDIED BY ONDOV, et al.

	Unit 1	Unit 2	Unit 3
Generating Capacity (MW)	185	240	750
Coal Size and Firing Mode	Pulverized Coal, Front Fired	Pulverized Coal, Front Fired	Pulverized Coal, Front and Rear Fired
Particulate Control System	Venturi Scrubber	Venturi Scrubber	Cold-Side Electrostatic Precipitator
Particulate Collector Efficiency (%)	99.2	99.2	97
Boiler Efficiency (%)	87	87	88.7
Maximum Continuous Steam Capacity (kg/sec)	160	203	654
Excess Air (%)	15	12.5	16

SOURCE: Ondov, et al. (1).

5.1.2 Studies of Trace Element Pathways Through the T.A. Allen Steam Plant

The atmospheric emissions listed for the Thomas A. Allen Steam Plant in Memphis, Tennessee, are part of the results of a series of interrelated, interdisciplinary studies carried out on this plant. These studies were carried out by several groups from the Oak Ridge National Laboratory. The results of these studies have been summarized by Lyon (2). Many of the results were previously reported in a variety of presentations, reports and publications (6-18). Slight differences exist among these reports concerning emission rates. In case of conflict, the values presented by Lyon (2) are given.

The Thomas A. Allen Steam Plant is part of the Tennessee Valley Authority (TVA) electrical generating system. The plant was built in 1956 to 1959. The plant consists of three similar cyclone fired boilers. Each unit has a generating capacity of 290 MW(e). Samples were taken around the Number 2 Unit. Two sets of samples were taken, the first in January 1972 and the second in August 1973. Impinger solutions were used during the 1973 sampling effort to measure elements leaving the plant in the vapor phase. The impinger solutions were analyzed for antimony, arsenic, selenium, and mercury. Each set of samples represented several days of plant operation. A new high efficiency electrostatic precipitator had been installed on the Number 2 Unit just before the first set of samples were taken. Operating parameters for the plant during the sampling periods are listed in Table 5-4.

Elemental flows and mass balance data are presented for 38 elements. Mass balances for five of these elements showed serious imbalance. Chlorine and bromine exhibited serious negative imbalance indicating that these elements were escaping as vapors. Impinger solutions were not analyzed for these elements. Serious positive imbalances were observed for chromium and vanadium. Lyon speculated that corrosion of boiler tubes might be responsible. Arsenic exhibited large negative imbalances for one sample set and large positive imbalances for the other. Sampling and analytical difficulties were blamed for the arsenic imbalances. The standard deviation from balance of the remaining mass balances was 15 percent.

TABLE 5-4. OPERATING CONDITIONS FOR THE T.A. ALLEN STEAM PLANT

	January 1972	February 1973
Heating value of coal (joules/g)	24,960	26,480
Operating level (MW)	240	280
Coal flow rate (g/min)	1.24×10^6	1.47×10^6
Slag flow rate (g/min)	1.33×10^5	8.43×10^4
Inlet Fly ash (g/min)	5.50×10^4	7.39×10^4
Outlet fly ash (g/min)	1,900	370
Precipitation efficiency (%)	96.5	99.5

SOURCE: Lyon (2)

Instrumental neutron activation analysis was used for the measurement of the concentration of most of the elements. Other analytical techniques used were:

- isotope dilution spark source mass spectrometry,
- flameless atomic absorption,
- gas chromatography with microwave emission spectrometric detector, and
- X-ray fluorescence.

See Chapter 8 for a full explanation of these techniques.

5.1.3 Studies of Trace Element Emissions from Coal-Fired Steam Plants Equipped with Hot-Side and Cold-Side Electrostatic Precipitators for Particulate Control

Mann et al. (3) reported the results of a study of trace element emissions from two power plants using pulverized Wyoming sub-bituminous coal. Both plants had tangentially fired boiler configurations. Although both coals were of the same type, they differed in moisture and ash content and in heating value. In one plant, particles were controlled by a hot-side electrostatic precipitator and in the other plant particulates were controlled by a cold-side electrostatic precipitator. The hot-side electrostatic precipitator operated at approximately 370°C (700°F) and the cold-side electrostatic precipitator operated at about 120°C (250°F).

To measure emissions to the atmosphere, particles and vapors were collected downstream from the electrostatic precipitators. The sampling devices employed were cyclones backed up by wet electrostatic precipitators. The collected particles and vapors were analyzed for up to 15 elements. Emissions to the atmosphere were reported for 13 elements. These emissions are listed as percentages of the elements entering with the coal in Table 5-5.

TABLE 5-5. PERCENTAGES OF ELEMENTS ENTERING WITH THE COAL WHICH WERE EMITTED TO THE ATMOSPHERE FROM TWO WESTERN COAL-FIRED POWER PLANTS

	Hot-Side Station	Cold-Side Station
Arsenic	10.0	0.7
Beryllium	1.0	0.6
Cadmium	2.2	0.7
Chromium	2.4	0.8
Copper	4.3	7.1
Fluorine	16.5	33.9
Manganese	1.8	0.7
Mercury	14.3	22.3
Nickel	3.6	1.3
Selenium	16.7	0.9
Titanium	2.5	0.2
Uranium	2.3	0.4
Zinc	3.1	18.8
Ash	2.6	0.3

SOURCE: Mann *et al*. (3)

5.1.4 Trace Element Emissions from Three Western Coal-Fired Power Plants

Radian Corporation (4) has reported mass balances for 27 trace elements around 3 western coal-fired power plants. Samples were taken simultaneously for all streams entering and leaving each unit sampled for a two-day sampling period at each plant. A unit consisted of a boiler and its associated particle control device. Very fine particles and elements in the vapor phase in effluent gases were collected with the aid of a wet electrostatic precipitator. Mercury vapor was collected from the effluent gas on a plug of gold wire.

Station I consisted of four units with a total capacity of 750 MW. Unit No. 4 was sampled. This unit had a tangentially fired balanced draft boiler and an electrical generating capacity of 330 MW. Three venturi scrubbers provided particulate emission control. The boiler was fired with Wyoming sub-bituminous coal mined near the station. Bottom ash was sluiced to a nearby settling pond. The scrubber slurry discharge was pumped to the same pond.

The coal contained 27.0 percent moisture, 15.0 percent ash, 31.1 percent volatile matter, 0.52 percent sulfur and 16.15×10^6 joules per kg (6948 Btu per pound) on an as received basis. The coal was fed at the rate of 1.28 x 10 kg per hr (2.83×10^5 lb per hr).

Elemental flows were calculated by multiplying the elemental concentration in a stream by the flow rate of the stream. The elemental flow rates for all streams entering the unit were added up and the elemental flow rates for all streams leaving the unit were added up. Error limits were determined for all measurements of elemental concentrations and stream flow rates. An error propagation analysis was carried out to determine the error in elemental flow rates entering and leaving the unit. These errors were given at the 95 percent confidence level. If the error band for the flow rate of an element entering the unit overlapped with the error band of that element leaving the unit the material balance was said to close.

Material balances were achieved within estimated error limits for 24 of the 27 elements measured. The material balances did not close within the preset error limits for cadmium, lead and mercury. The ratio of the elemental flow rate leaving the unit to element flow rate entering the unit (for those elements achieving material balance closure) ranged from 0.80 for beryllium to 1.38 for zinc. The root mean square of normalized deviations from material balance closure was 24 percent. This value included deviations for those elements which did not achieve material balance closure.

Station II was a 350 MW unit with a tangentially fired boiler. The coal was pulverized before firing. Pyrites were removed from the pulverized coal at the mill. Bottom ash, economizer ash and pyrites from the pulverizing mill were sluiced to a settling pond. Particles were controlled with hot-side electrostatic precipitators. Ash collected in the precipitators was trucked from the plant site.

Wyoming sub-bituminous coal was used as fuel. Coal analysis for Station II was 29.2 percent moisture, 5.12 percent ash, 0.35 percent sulfur and 19.27×10^6 joules per kg (8290 Btu per lb) on an as-received basis. Coal was fed at a rate of 1.25×10^5 kg per hr (2.75×10^5 lb per hr).

Elemental flow rates were given for all streams entering and leaving the unit. Material balances were calculated as described above for Station I. Material balances were achieved for 23 of the 27 elements measured. Material balances were not achieved for chlorine, mercury, selenium and uranium. The root mean square of normalized deviations from material balance closure was reported to be 48 percent. This value included deviations for those elements which did not achieve material balance closure.

Station III was a 250 MW cyclone fired unit. North Dakota lignite was the fuel. Bottom ash and economizer ash were sluiced to a nearby pond. Particles were controlled with cyclones (mechanical collectors). The lignite analysis was reported to be: 36.8 percent moisture, 7.84 percent ash, 0.91 percent sulfur and 14.44×10^6 joules per kg (6214 Btu per lb) on an as-received basis. It was fired at a rate of 1.06×10^5 kg per hr (2.34×10^5 lb per hr).

Material balances closed within error limits for 21 of the 27 elements measured. Material balance closure within limits was not achieved for cobalt, chlorine, mercury, molybdenum, selenium or uranium. The root mean square of normalized deviations from material balance closure was reported to be 37 percent. This value included deviations for those elements which did not achieve material balance closure.

Analytical techniques used for the three-station study were:

- atomic absorption,
- X-ray fluorescence,
- ion selective electrodes,
- fluorometry,
- spectrometry, and
- spark source mass spectrometry.

The first five methods were reported to yield significantly better material balance closure and repeatability of duplicate analyses than spark source mass spectrometry.

5.1.5 Trace Element Emissions from TVA's Widows Creek Power Plant

Cowherd et al. (5) reported the results of a trace element study carried out at the Widows Creek Steam Electric Power Plant. This plant is part of the Tennessee Valley Authority's (TVA) electric generating network. Unit 5 of this plant was selected for the test program. The Widows Creek station is five miles southwest of Bridgeport, Alabama.

Unit 5 was put into commercial operation in 1954. The unit fired pulverized coal in a dry bottom furnace. The generating capacity of this unit was 125 MW. Particulates were controlled with a mechanical fly ash collector (two four-bank multiclone units were used). Bottom ash was sluiced from the ash hopper. Samples were collected over a nine-day period in August, 1974.

Pollutant mass flow rates were given for 23 elements. Mass balances were within ±25 percent for about half of these elements. The authors reported large negative mass imbalances ascribed to inefficient pollutant collection for the following elements: antimony, arsenic, fluorine, mercury, and selenium.

5.2 ATMOSPHERIC TRACE ELEMENT EMISSIONS FROM COAL-FIRED POWER PLANTS; VALUES NOT BASED ON HEATING VALUE IN COAL

Several studies have been reported in addition to those given in Section 5.1. These studies reported emissions in a variety of ways but did not provide enought information to calculate emissions on the heating value basis presented in Tables 5-1 and 5-2. These studies are described below.

5.2.1 Trace Element Emissions to the Atmosphere from the Valmont Power Station, Boulder, Colorado

Kaakinen *et al*. (19) (also 20, 21, 22) reported the partitioning of 17 elements in the Valmont Power Station. Flow rates and elemental concentrations were given so absolute elemental flows and emission rates could be calculated. The heating value of the coal was not given. An assumption would have to be made concerning the efficiency of the unit sampled to calculate emissions normalized to the heating value of the coal. Mass balances were reported for 12 of the elements measured.

The measurements were taken at Unit Number 5 of the Valmont Power Station belonging to Public Service Company of Colorado. This plant is near Boulder, Colorado. The coal used was from a single mine and contained about 0.6 percent sulfur and 6 percent ash. The coal was pulverized before it was fired. The capacity of the Unit Number 5 is 180 MW (net).

Three types of particulate collection devices were being used on this plant when the samples were collected.

All of the flue gas from the boiler passed through a mechanical dust collector (cyclone). The mechanical collector removed approximately 86 percent (by weight) of the particles from the flue gases. The partially cleaned stream was split. Approximately half of the stream passed through an electrostatic precipitator and the other half passed through a wet scrubber.

Concentrations of 11 elements were given for eight streams in the plant. The eight streams were: the coal entering the plant, the scrubber inlet stream, and six streams leaving the plant. Four more elements were measured in some of the streams. The BET (see Glossary) surface area of the particles from several of the streams leaving the plant was measured.

Analytical methods used were:

- atomic absorption spectrophotometry (conventional and flameless),
- wet chemistry, and
- X-ray fluorescence.

Three radioactive isotopes were measured using radiochemical analysis.

Mass balances were poor for selenium and mercury. These elements were thought to escape as elemental vapors.

Kaakinen et al. referred to work by Bethell (23) who was said to have reported that the calcium concentration in the coal would influence the volatility of arsenic in the coal. In high calcium coals arsenic was said to be largely retained as arsenate/arsenite. But, in low calcium coals the arsenic was said to be volatilized as arsenic trioxide.

5.2.2 Trace Element Concentrations in Materials from the Chalk Point Electric Generating Station

Gladney et al. (24) have reported trace element concentrations in materials from the Chalk Point Electric Generating Station in southeastern Maryland. Concentrations in coal, precipitator ash and fly ash passing through the electrostatic precipitator were reported. Fly ash particles were collected using a University of Washington Mark III Cascade Impactor. Elemental concentrations were reported for each of the seven collecting stages and the back-up filter. Flow rates were not given so emissions rates could not be calculated. Only particles were collected; no information about trace elements in the vapor phase was reported.

The Chalk Point Electric Generating Station is operated by the Potomac Electric Power Company. At the time the samples were taken the plant consisted of two 355 MW generators each consuming 10^5 kg of coal per hour at full load. The coal is ground to 50 mesh and blown from the pulverizer into the water wall furnace. The coal is mined in West Virginia and Pennsylvania.

The authors reported the following distribution of ash: bottom slag, 9 percent; economizer ash, 12 percent; precipitator ash, 75 percent; fly ash to atmosphere, 4 percent. The temperature in the combustion zone was reported to reach 1600°C. The gas at the outlet of the economizer was reported to be 450°C. The temperature at the inlet to the electrostatic precipitator was reported to be 130°C and the temperature at the outlet of the electrostatic precipitator was 120°C.

Gladney *et al*. reported that their observed instack elemental distributions with particle size did not match ambient particle size distributions observed for trace elements in urban areas. They suggested that if the emissions from other coal plants were similar to those observed at Chalk Point, emissions from coal-fired installations do not have a major impact on observed urban trace element concentrations.

All samples were analyzed non-destructively by instrumental neutron and photon activation analysis. Mercury was determined using a combustion procedure and was measured on only one set of samples.

5.2.3 Beryllium Emissions to the Atmosphere from the Chalk Point Electric Generating Station

Gladney and Owens (25), in a study related to the one discussed in Section 5.2.2, reported values for atmospheric emissions and mass balances for beryllium.

Samples were collected for nine days in August, 1973, from the Chalk Point Electric Generating Station. Suspended particles which had passed through the electrostatic precipitator used for particulate emission control were collected with a University of Washington Mark III Instack Cascade Impactor.

Measurements were made on bottom slag, economizer ash, precipitator ash and/or particles collected downstream from the electrostatic precipitator. Aluminum was used as an internal reference for normalizing data. Slight enrichments of beryllium relative to aluminum were observed for all of the ashes collected in the plant. The particles collected downstream from the electrostatic precipitator showed a slight overall depletion in beryllium although they exhibited increasing beryllium concentration with decreasing particle size.

Beryllium concentrations were measured with a flameless atomic absorption method developed especially for handling refractory samples such as fly ash.

The authors concluded that no more than 4 or 5 percent of the beryllium present in the coal was leaving with the fly ash leaving the plant. The authors noted several inconsistencies in the beryllium analyses reported by Phillips (26).

5.2.4 Airborne Beryllium and Beryllium in Coal at the Hayden Power Plant Near Hayden, Colorado

Phillips (26) reported the results of chemical analysis of a composite coal sample and a composite fly ash sample from the Hayden Power Plant near Hayden, Colorado. Based on these two samples 84 percent of the beryllium entering the plant with the coal was calculated to be emitted to the atmosphere. Spark source mass spectrometry was the analytical method used for these analyses. On a separate occasion a sample of airborne particulate matter was collected near the plant. An ambient beryllium concentration of 0.004 μg per cubic meter was calculated based on the analysis of the particles collected.

Gladney and Owens (25) have pointed out internal inconsistencies and possible sources of analytical error in Phillips' report.

5.2.5 Trace Element Emissions From a Coal-Fired Power Plant in Illinois

Lee et al. (27) reported measurement of trace element emissions from a coal-fired power plant in Illinois. No attempt was made to calculate trace element balances around the plant.

The generating capacity of the power plant was 105 MW. Sixty tons (54 Mg) of coal per hour were fed to the unit. Coal characteristics were not given. The stack gas flow rate was 7273 m^3 per minute (dry basis).

Particulate emissions were controlled by an electrostatic precipitator with a rated efficiency of 99.7 percent. The total particulate emissions of the power plant were reported to be 2364 g per minute. Of the particulate emissions, 284 g per minute were reported to be in the submicron size range.

Particle matter was collected using a University of Washington Mark III Cascade Impactor. Collected materials were ashed in a low temperature asher and dissolved in 1:1 nitric acid. The solution obtained was analyzed for antimony, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, vanadium, and zinc. Analysis was by atomic absorption spectrophotometry in a graphite furnace. Table 5-6 lists the concentrations of trace elements in the particulate emissions to the atmosphere.

5.2.6 Total Mercury Mass Balance at a Coal-Fired Power Plant

Kalb (28) has reported the results of a series of test runs to measure mass balances for mercury around a coal-fired power plant. The power plant studied was built in 1949, had an output of 93 MW and fired pulverized coal. Particles were controlled by two mechanical collectors in series and an electrostatic precipitator. The mechanical collectors were reported to be 40 percent efficient and the electrostatic precipitator was reported to be 91 percent efficient.

The results of 14 test runs showed that:

- some of the mercury was not volatilized during combustion,
- about 10 percent of the volatilized mercury was recovered by adsorption onto suspended ash particles,
- some of the mercury was removed from the system by adsorption onto the walls of stacks and ducts, and
- the major portion of the volatilized mercury was released to the atmosphere in the vapor phase.

5.2.7 Other Studies of Trace Element Emissions from Coal-Fired Facilities

Stephens *et al*. (29) analyzed samples of pulverized coal, fly ash, bottom ash and ash pond liquid and ash pond sediments for a number of trace elements. Analytical methods used were neutron activation analysis and

TABLE 5-6. CONCENTRATION OF TRACE ELEMENTS IN PARTICULATE EMISSIONS TO THE ATMOSPHERE FROM A COAL-FIRED POWER PLANT IN ILLINOIS

Elements	Concentration (μg/m)	Mass Median Diameter of Particles Bearing Element (μm)
Antimony	6.8	0.6
Cadmium	0.1	5.0
Chromium	0.7	<0.5
Iron	1340.	2.6
Lead	1.4	1.1
Manganese	0.0	---
Nickel	1.3	5.4
Vanadium	1.5	1.6
Zinc	0.7	4.7
Total Particulate Matter	8700.	4.7
Selenium[1]	6.5	4.7
Total Particulate Matter[1]	9600.	4.7

[1] Selenium was analyzed on a separate sample set using neutron activation analysis.

SOURCE: Lee *et al*. (27)

atomic absorption spectrophotometry. A mass balance was attempted to determine the emission points in the combustion process.

Rancitelli (3) calculated emissions of 12 elements from the Hanford Steam Plant in 1971. He reported that chromium, iron, sodium and rubidium were conserved, but found that antimony, mercury and selenium were depleted in ash relative to the coal. He calculated emissions based on the depletions observed. Neutron activation analysis was the analytical method used.

Carter *et al*. (31) reported mass balance results around a coal-fired electric generating plant. Thermal emission, spark source and isotope dilution mass spectrometry were the analytical methods used. These results were reported in 1973.

Schultz (32, 33) has reported on the fate of trace elements during coal pretreatment and combustion.

5.3 TRACE ELEMENT EMISSIONS VIA SOLID WASTES OR AQUEOUS EFFLUENTS FROM COAL-FIRED FACILITIES

Trace elements enter a coal combustion facility with the coal. If they are not emitted to the atmosphere they must leave with solid wastes or with aqueous effluents. Since solid wastes and aqueous effluents are often combined with each other, they will be considered together.

The major solid waste streams from a coal-fired facility are ashes and wastes from throwaway type flue gas desulfurization (FGD) systems. Ashes commonly collected at a coal-fired facility include bottom ash or slag plus fly ash collected in the economizer, mechanical collector, electrostatic precipitator and/or wet scrubber.

Most utilities dispose of their solid wastes by ponding or by landfill. Ponding is a disposal method in which the waste material is wet when it enters the pond. Impoundments or other restraints are required for mechanical stability. In this chapter landfill will be defined to mean any waste disposal operation in which the waste material has enough structural integrity throughout the disposal site that impoundments or other structural supports are unnecessary.

Ponding is widely used by utility companies. Often ponding is used for temporary storage. When the pond is nearly full of solid material it is allowed to dry and the solid waste is removed to a landfill for permanent disposal. Ponds may contain only one type of waste or they may contain a mixture of coal-related solid wastes.

In many cases supernatant liquor from the pond or ponds is recycled to the power plant. The recycled liquor may be used as ash sluice water or as scrubber make-up water. In other cases the pond overflow enters the environment via the nearest stream. Of course, partial recycle and partial discharge of pond liquors is possible.

In many cases physical or chemical properties of the waste are not compatible with immediate or permanent use in a landfill site. In these cases ponding must be used for permanent disposal.

Many utility companies choose to dispose of some solid wastes directly in landfills. It is not unusual for a plant to truck precipitator ash and/or economizer ash to a landfill site and to sluice bottom ash to a pond. Flue gas desulfurization sludges are usually ponded, at least initially.

Aqueous effluents can be divided into two classes. In the first class the emission points are usually well defined streams. These emissions usually result directly from the day to day operation of the facility. These effluents include discharges such as once through cooling water and pond overflows. These effluents usually enter surface waters.

The other class of aqueous effluent enters the environment from more dispersed sources. This class includes surface run-off from landfill operations, run-off and leachate from ponds and landfill operations. There effluents may enter either surface waters or ground water.

Reports dealing with trace element emissions associated with solid wastes or aqueous effluents are discussed below. This section contains discussions of emissions associated with solid wastes and well defined aqueous streams. The next section deals with run-off and leachates.

5.3.1 The Impact of RCRA on Utility Solid Wastes

Hart et al. (34) have prepared an extensive review of the impact of the Resource Conservation and Recovery Act of 1976 on utility waste disposal practices. Utility solid and liquid waste streams were categorized with respect to environmental hazard potential. Comparisons were made between proposed hazardous waste criteria and reported composition of various waste streams. Processes which were reported to produce waste streams which could exceed the criteria were presumed to be a candidate for regulation under the act.

The first category identified was waste streams having the greatest hazard potential. These streams were considered most likely to be included on a presumptive process list. Streams belonging to this category were:

- coal fly ash,
- coal bottom ash, and
- FGD scrubber sludge.

The second category was waste streams which are possibly hazardous. It was considered possible that these streams might be included on a presumptive process list:

- metal cleaning wastes from boiler generator tubes, boiler fireside, and air preheater,
- coal pile drainage,
- boiler blowdown,
- recirculating condenser cooling system wastes,
- oil fly ash, and
- ion exchange wastes.

The third category included least hazardous wastes. It was considered unlikely that these wastes would be included on a presumptive process list. Wastes in this category were:

- water treatment wastes and
- once through condenser cooling system wastes.

See Chapter 4 for an explanation of these waste streams.

Hart et al. reported information available from the literature. This report is a convenient source of information from diverse sources; however, sometimes information from several sources has been combined into a single table and it is not possible to associate a particular piece of information with a given source.

The constituents of coal-pile run-off as compiled by Hart et al. are listed in Table 3-7. The data in this table were obtained from three original sources: Cox and Ruane (35), Rice and Strauss (36), and USEPA (37).

5.3.2 Review and Assessment of the Existing Data Base Regarding Flue Gas Cleaning Wastes

Coltharp et al. (38) have prepared an extensive review of information regarding flue gas cleaning wastes. Flue gas cleaning wastes include fly ash, flue gas desulfurization (FGD) sludge, mixtures of fly ash and sludge, aqueous solutions associated with the solids at time of disposal and leachates from the solids. The review covers information available from the open literature and from persons working in the field through mid-1977. The available information was critically assessed and data gaps identified.

The appendix to the Coltharp report contains a comprehensive compilation of the public information concerning flue gas cleaning wastes available at the time the report was prepared. It provides another convenient source (in addition to that provided by Hart et al.) for these data. References are given in such a way that the original sources of all data presented can be identified.

Some of the data presented in the Coltharp report are presented with discussions of individual projects below. Table 5-8 presents concentrations of trace elements in liquors adhering to the sludge (sludge liquor) and in solutions obtained when additional water was passed through the sludge (elutriates). The data were taken from three sources as reported by Coltharp et al.

TABLE 5-7. CONSTITUENTS OF COAL PILE RUNOFF

	Range (mg/l)
Conventional Measures of Pollution	
pH	2.1 - 6.6
Total Suspended Solids	22. - 610.
Total Dissolved Solids	720. - 28,970.
Turbidity	2.77 - 505.
Total Hardness	130. - 1,851.
Major Chemical Constituents	
Ammonia	0.0 - 1.77
Nitrate	0.3 - 1.9
Phosphorus	0.2 - 1.2
Sulfate	130. - 20,000.
Chloride	3.6 - 481.
Aluminum	66. - 1,200.
Iron	0.06 - 4,700.
Manganese	90. - 180.
Sodium	160. - 1,260.
Trace Element Constituents	
Arsenic	0.005 - 0.6
Beryllium	< 0.01 - 0.07
Cadmium	< 0.001 - 0.003
Chromium	0.0 - 16.
Cobalt	0.025 - --
Copper	0.01 - 3.9
Magnesium	0.0 174.
Mercury	< 0.0002- 0.007
Nickel	0.24 - 0.75
Selenium	< 0.001 - 0.03
Zinc	0.006 - 12.5

SOURCE: Hart *et al.* (34): Original sources were Cox and Ruane (35), Rice and Strauss (36) and USEPA (37).

TABLE 5-8. SUMMARY OF CONCENTRATIONS OF TRACE ELEMENTS SLUDGE LIQUORS AND ELUTRIATES

	Holland, and Jones		Rossoff and Rossi				Bornstein	All Sources
			Eastern Coal		Western Coal			
Element	Range, (mg/1)	Mean, (mg/1)	Range, (mg/1)	Median, (mg/1)	Range, (mg/1)	Median, (mg/1)	Range, (mg/1)	Range, (mg/1)
Aluminum	--	--	--	--	--	--	0.03 to 0.3	0.03 to 0.3
Antimony	0.09 to 2.9	0.2	0.46 to 1.6	1.2	0.09 to 0.22	0.16	0.09 to 2.3	0.09 to 2.9
Arsenic	0.004 to 0.3	0.009	< 0.004 to 1.8	0.02	< 0.004 to 0.2	0.009	< 0.004 to 0.3	< 0.004 to 0.3
Beryllium	0.0006 to 0.14	0.013	< 0.0005 to 0.05	0.014	0.0006 to 0.14	0.013	< 0.002 to 0.14	< 0.0005 to 0.14
Boron	0.9 to 46	--[1]	41	41	8.0	8.0	8.0 to 46	0.9 to 46
Cadmium	0.002 to 0.044	0.032	0.004 to 0.1	0.023	0.011 to 0.044	0.032	0.004 to 0.11	0.002 to 0.11
Chromium	0.005 to 0.4	0.08	0.001 to 0.5	0.02	0.024 to 0.4	0.08	0.01 to 0.5	0.001 to 0.5
Cobalt	0.1 to 0.7	--	< 0.002 to 0.1	0.35	0.1 to 0.17	0.14	0.10 to 0.7	< 0.002 to 0.7
Copper	0.002 to 0.6	0.20	0.002 to 0.4	0.015	0.002 to 0.6	0.20	< 0.002 to 0.2	< 0.002 to 0.6
Fluorine	0.7 to 3.0	1.5	1.4 to 70	3.2	0.7 to 3.0	1.5	--	0.7 to 70
Iron	0.02 to 8.1	--[1]	0.02 to 0.1	0.026	0.42 to 8.1	4.3	0.02 to 8.1	0.02 to 8.1
Lead	0.001 to 0.4	0.016	0.002 to 0.55	0.12	0.0014 to 0.37	0.016	0.01 to 0.4	0.001 to 0.55
Manganese	0.007 to 2.5	< 0.74	< 0.01 to 9.0	0.17	0.007 to 2.5	0.74	0.09 to 2.5	0.007 to 9.0
Mercury	0.0004 to 0.07	< 0.01	0.0009 to 0.07	0.001	< 0.01 to 0.07	0.01	0.0004 to 0.07	0.0004 to 0.07
Molybdenum	0.07 to 6.3	--[1]	5.3	5.3	0.91	0.91	0.91 to 6.3	0.07 to 6.3
Nickel	0.005 to 1.5	0.09	0.03 to 0.91	0.13	0.005 to 1.5	0.09	0.05 to 1.5	0.005 to 1.5
Selenium	0.001 to 2.2	0.14	0.005 to 2.7	0.11	< 0.001 to 2.2	0.143	< 0.001 to 2.2	< 0.001 to 2.7
Silver	0.005 to 0.6	--[1]	--	--	--	--	0.005 to 0.6	0.005 to 0.6
Tin	3.1 to 3.5	--[1]	--	--	--	--	3.1 to 3.5	3.1 to 3.5
Vanadium	0.001 to 0.67	--[1]	--	--	--	--	0.001 to 0.67	0.001 to 0.67
Zinc	0.03 to 2.0	0.18	0.01 to 27	0.046	0.028 to 0.88	0.18	0.01 to 0.35	0.01 to 27

[1] Data were not available for calculation of a mean.

SOURCE: Holland and Jones (39); Rossoff and Rossi (40); Bornstein (41).

5.3.3 Trace Element Emissions in Solid Wastes and Aqueous Effluents from Three Western Coal-Fired Power Plants

Radian Corporation (4) has reported trace element concentrations in coal, ashes and sluice waters from three western power plants. These plants were described in Section 5.1.4. Trace element concentrations are listed in Tables 5-9, 5-10, and 5-11. The flow rates for the streams listed in these tables are given in Tables 5-12, 5-13, and 5-14. The amount of the element emitted per unit time can be calculated by multiplying concentration of the element in a stream by the flow rate of the stream.

5.3.4 Comparison of Levels of Trace Elements Extracted from Fly Ash and Levels Found in Effluent Waters from a Coal-Fired Plant

Dreesen et al. (42) determined concentrations of 11 trace elements in precipitator ash and in waters entering and leaving a western coal-fired power plant. The plant was located near Fruitland, New Mexico, and by implication had both electrostatic precipitators and venturi scrubbers for pollution control. Concentrations of trace elements in waters entering and leaving the plant are listed in Table 5-15.

A number of extraction experiments were carried out. In these experiments precipitator ash was extracted with a number of acidic, neutral and alkaline extractants. The results of the extraction study are presented in Table 5-16. It should be noted that redistilled water was one of the extractants. The water started out at a neutral pH but the alkalinity of the fly ash increased the pH to 11.9 at the end of the extraction.

Elements found to be most extractable in water were boron, fluorine, molybdenum and selenium. Elements most extractable in acid were arsenic, boron, cadmium, fluorine, molybdenum and selenium. Elements most elevated in effluent waters were arsenic, boron, molybdenum and selenium. The authors noted a positive correlation between readily extractable elements and elements elevated in effluent waters.

Dreesen et al. also noted that the elements most extractable in acids were among those reported to be concentrated on the surfaces of fly ash particles. A second factor which the authors discussed was that elements

TABLE 5-9. TRACE ELEMENT CONCENTRATIONS IN COAL, ASHES, AND AQUEOUS SAMPLES ASSOCIATED WITH A WESTERN COAL-FIRED POWER PLANT (STATION I)[1]

	Coal (µg/g)	Bottom Ash (µg/g)	Bottom Ash Sluice Water (mg/ℓ)	Scrubber Slurry Solids (µg/g)	Scrubber Slurry Liquid (mg/ℓ)	Clear Pond Return (mg/ℓ)
Aluminum	23,000.	103,000.	2.4	108,000.	4.8	5.0
Antimony	.53	.39	.041	2.3	0.36	.024
Arsenic	.83	1.3	.0041	5.2	.0013	.0045
Barium	130.	670.	<.5	840.	<.5	<.5
Beryllium	.82	2.5	.0013	3.2	.0015	.0013
Boron	51.	160.	2.5	220.	2.8	3.2
Cadmium	.18	1.0	.0038	1.8	.0068	.0054
Calcium	17,600.	86,600.	790.	113,000.	910.	790.
Chlorine	44.	140.	28.	89.	28.	28.
Chromium	21.	67.	.12	118.	.14	.074
Cobalt	2.1	7.0	.005	8.1	.011	.0081
Copper	34.	93.	.024	155.	.049	.036
Fluorine	140.	100.	16.	820.	20.	20.
Iron	4,000.	25,100.	.30	22,500.	.74	.31
Lead	4.2	7.1	.007	49.	.023	.008
Manganese	170.	690.	.79	1,000.	.88	.86
Magnesium	2,900.	12,000.	68.	13,600.	62.	68.
Mercury	.13	.014	<.0005	.053	.0007	<.0005
Molybdenum	4.0	3.7	.056	10.	.015	.035
Nickel	9.0	39.	.015	38.	.015	.025
Selenium	2.2	.70	.031	8.7	.12	.048
Titanium	1,100.	4,500.	<.1	4,000.	<.1	<.1
Silver	.045	.11	.0004	.23	.0005	.0003
Sulfur	7,200.	.11	770.	14,400.	865.	785.
Uranium	1.3	13.	.0058	3.6	.0087	.010
Vanadium	51.	230.	.19	268.	.23	.16
Zinc	24.	41.	.076	190.	.089	.10

[1] Values represent average of duplicate determinations: Coal was reported to be 20.62 percent ash on a dry basis.
SOURCE: Radian, Volume II, (4).

TABLE 5-10 TRACE ELEMENT CONCENTRATIONS IN COAL, SLUICE ASH , AND AQUEOUS SAMPLES FROM A WESTERN PULVERIZED COAL-FIRED POWER PLANT (STATION II)[1]

	Coal (µg/g)	Inlet Sluice Water (mg/l)	Sluice[2] Ash (µg/g)	Sluice Ash Filtrate (mg/l)
Aluminum	7,100.	< .1	109,000.	9.2
Antimony	.16	.0023	<.08	.0038
Arsenic	2.5	<.0001	1.4	<.0001
Barium	460.	<.6	5,200.	<.6
Beryllium	.29	<.002	4.1	<.002
Boron	31.	.17	240.	.49
Cadmium	<.1	<.002	<.8	<.002
Calcium	10,900.	57.	151,000.	113.
Chlorine	9.4	8.6	<1.	15.
Chromium	9.3	<.053		<.053
Cobalt	1.5	<.003	18.	<.003
Copper	31.	.012	230.	.022
Fluorine	67.	.45	19.	.70
Iron	2,100.	.12	40,600.	.01
Lead	2.3	.017	11.	.006
Manganese	24.	.034	310.	.016
Magnesium	1,500.	15.	20,600.	16.
Mercury	.14	.08	<.010	<.0004
Molybdenum	.64	<.0002	3.5	.015
Nickel	2.1	<.02	27.	<.02
Selenium	1.6	.0017	.35	.0038
Titanium	565.	<.1	9,100.	<.1
Silver	.048	<.0003	.11	<.0003
Sulfur	4,900.	14.	910.	108.
Uranium	.89	.0084	5.0	.0044
Vanadium	20.0	0.058	190	0.071
Zinc	4.1	.39	156.	.0084

[1] Values represent the average of duplicate determinations. The coal was reported to be 7.23 percent ash on a dry basis.

[2] Sluice ash is a combination of bottom ash, economizer ash, and pyrites from the mills which pulverize the coal

SOURCE: Radian, Volume III, (4).

TABLE 5-11 TRACE ELEMENT CONCENTRATIONS IN COAL, ASH, AND AQUEOUS STREAMS FROM A WESTERN CYCLONE TYPE COAL-FIRED POWER PLANT (STATION III)[1]

Element	Coal (μg/g)	Ash Sluice Water Inlet (mg/l)	Bottom Ash (μg/g)	Bottom Ash Sluice Water (mg/l)	Economizer Ash (μg/g)	Economizer Ash Sluice Water (mg/l)
Aluminum	7400.	.42	87900.	1.7	84800.	.58
Antimony	.40	.018	.8	.034	.56	.021
Arsenic	8.0	.006	20.	.0087	126.	.0012
Barium	440.	<.5	5700.	< .5	8300.	<.5
Beryllium	.60	.0014	5.3	.0017	8.8	.003
Boron	150.	.26	520.	.25	740.	2.4
Cadmium	.20	.0003	.87	.0011	1.8	.0012
Calcium	13800.	35.	130000.	43.	120000.	46.
Chlorine	55.	12.	88.	16.	119.	17.
Chromium	13.	<.053	95.	< .053	121.	<.053
Cobalt	.75	.0003	10.	.0041	12.	.0039
Copper	10.5	.0084	50.	.014	94.	.008
Fluorine	57.	.21	<10.	.25	65.	.21
Iron	7500.	.43	664000.	2.1	66900.	1.4
Lead	.86	.015	< .8	.024	8.3	.025
Magnesium	3700.	26.	37100.	26.	37700.	24.
Manganese	79.	.082	720.	.055	900.	.096
Mercury	.074	<.0005	< .010	< .0005	.12	<.0005
Molybdenum	2.0	.033	18.	.016	44.	.012
Nickel	5.4	.006	23.	.0014	36.	.007
Selenium	1.3	.0012	.25	.0011	.14	.0012
Titanium	350.	<.1	3500.	< .1	3800.	<.1
Silver	.034	<.0003	.11	< .00003	.32	<.0003
Sulfur	14400.	68.	95.	74.	1300.	77.
Uranium	1.5	.0022	3.2	.0035	11.	.0044
Vanadium	15.	<.005	140.	< .005	110.	<.005
Zinc	7.8	.013	18.	.013	140.	.028

[1] Values represent the average of duplicate determinations. Coal was reported to be 12.40 percent ash on a dry basis.
SOURCE: Radian, Volume IV, (4)

TABLE 5-12. FLOW RATES FOR STREAMS AROUND STATION I

Stream	Flow Rate
Coal	1.28 x 10^5 kg/hr.
Bottom Ash Sluice Water Inlet	0.585 x 10^6 kg/hr.
Cooling Tower Blowdown	1.99 x 10^5 kg/hr.
Scrubber Make-up Water	1.81 x 10^6 kg/hr.
Lime	2.17 x 10^3 kg/hr.
Bottom Ash	0.522 x 10^4 kg/hr.
Bottom Ash Sluice Water Outlet	0.585 x 10^6 kg/hr
Scrubber Solids	2.27 x 10^4 kg/hr.
Scrubber Liquid	1.90 x 10^6 kg/hr.
Economizer Ash	11.9 kg/hr.
Flue Gas	1.42 x 10 m^3/hr
Fly Ash	74.8 x 10^2 kg/hr.

SOURCE: Radian, Volume I (4).

TABLE 5-13. FLOW RATES FOR STREAMS AROUND STATION II

Stream	Flow Rate
Coal	1.25×10^5 kg/hr.
Inlet Sluice Water	2.28×10^5 kg/hr.
Sluice Solids	2.0×10^3 kg/hr.
Sluice Liquid	2.28×10^5 kg/hr.
Precipitator Ash	6.94×10^3 kg/hr.
Flue Gas	1.55×10^6 m^3/hr.
Fly Ash	63.5×10^2 kg/hr.

SOURCE: Radian, Volume I, (4).

TABLE 5-14. FLOW RATES FOR STREAMS AROUND STATION III

Stream	Flow Rate
Coal	1.06×10^5 kg/hr.
Bottom ash and economizer ash sluice water inlet	1.20×10^5 kg/hr.
Bottom ash	7.62×10^3 kg/hr.
Bottom ash sluice water outlet	8.07×10^4 kg/hr.
Economizer ash	69.9 kg/hr.
Economizer ash sluice water outlet	3.95×10^4 kg/hr.
Cyclone ash	2.83×10^3 kg/hr.
Flue gas	1.16×10^6 m^3/hr
Fly ash	1.55×10^3 kg/hr.

SOURCE: Radian, Volume I, (4).

TABLE 5-15. TRACE ELEMENT CONCENTRATIONS IN WATER ENTERING AND LEAVING A WESTERN COAL-FIRED POWER PLANT

	Influent Waters		Effluent Waters	
Element	Cooling lake intake (μg/l)	Cooling lake outlet, (μg/l)	Ash pond effluent, (μg/l)	Ash pond surface, (μg/l)
Arsenic	2.6	7	27	33
Beryllium	<0.2	<0.2	<0.2	<0.2
Boron	<100	950	12000	11000
Cadmium	1	1	1	1
Chromium	<1	1	2	3
Copper	3	2	3	2
Fluorine	220	3700[1]	16000	ND[2]
Molybdenum	<1	23	170	160
Selenium	<1	1	57	60
Vanadium	2	60	130	140
Zinc	590	350	440	580

[1] Data for September 1975, from the New Mexico Environmental Improvement Agency. [2] No data.

SOURCE: Dreesen *et al*. (42)

TABLE 5-16 TRACE ELEMENT CONCENTRATIONS IN PRECIPITATOR ASH AND PERCENTAGE OF TRACE ELEMENT CONTENT OF ASH EXTRACTED BY SEVERAL EXTRACTING SOLUTIONS

Element	Conc. in Precipitator Ash (μg/g)		Amount of Each Element Extracted (%)							
		Molarity	1.0	1.0	0.1	0.1	0.01	0.001		0.1
		Solution	HNO_3	HCl	Citric Acid	HNO_3	HNO_3	HNO_3	H_2O	NH_4OH
		Initial pH[1]:	0.5	0.5	2.2	1.4	2.2	3.1	7.4	11.3
		Final pH[2]:	0.5	0.6	3.6	4.1	11.7	11.9	11.9	11.9
Arsenic	12		64	78	59	0.65	0.31	0.17	0.10	0.51
Beryllium	4.7		8.6	12	6.1	1.7	<0.09	<0.09	<0.09	<0.09
Boron	260		78	24	94	55	3.9	1.4	1.5	<0.05
Cadmium	0.29		48	32	33	35	3.8	0.28	<0.14	0.14
Chromium	34		15	14	13	1.2	0.53	0.38	0.33	0.29
Copper	58		7.3	7.9	4.6	3.3	0.11	<0.01	<0.01	<0.01
Fluorine	120[3]		75	63	86	83	11	8.1	7.2	8.7
Molybdenum	4.2		120	120	110	4.7	57	55	59	54
Selenium	8.0		78	35	46	5.1	11	5.9	5.1	4.5
Vanadium	98		20	28	16	0.04	0.02	<0.01	<0.01	<0.01
Zinc	160		3.1	3.1	1.8	1.2	0.27	<0.03	<0.03	0.07

[1] pH determined before ash was added to the extractants. [2] pH determined after agitation of ash-extractant mixture. [3] The fluorine concentration given is the mean concentration reported by the Southwest Energy Study (43, 44).

SOURCE: Dreesen (42)

which form anionic species remain soluble in alkaline environments. They suggested that molybdate, borate, fluoride, selenate, arsenate, chromate and vanadate could occur as soluble forms.

The authors were not able to tell whether the elements enriched in the effluent waters were dissolved in the acidic environment of the venturi scrubbers and not reprecipitated or if they were extracted under more alkaline conditions. They suggested that arsenic, boron, fluorine, molybdenum and selenium were elements of prime interest for future studies of soluble contaminants from coal ash disposal in alkaline environments.

5.3.5 Concentrations of Trace Elements in Ash Ponds at Coal-Fired Power Plants Operated by the Tennessee Valley Authority

Chu *et al*. (45) have reported trace element concentrations in ash ponds at coal-fired power plants operated by the Tennessee Valley Authority. The values reported are listed in Tables 5-17, 5-18, and 5-19.

Plants A, B, E, G, and I were reported to burn coal from Western Kentucky. Plants C, F, and K burned coal from Western Kentucky and Southern Illinois. Plant D burned coal from Eastern Kentucky. Plants H and J burned coal from Eastern Kentucky and Eastern Tennessee. Plant L burned coal from western Kentucky and Northern Alabama. Plants A and C employed cyclone firing. All other plants fired pulverized coal.

5.4 SECONDARY EMISSIONS OF TRACE ELEMENTS FROM SOLID MATERIALS ASSOCIATED WITH THE COMBUSTION OF COAL

This section addresses trace element emissions from run-off and leachates. These emissions generally do not occur as readily identifiable waste streams. Furthermore, emissions to the environment in leachates have the potential for occurring long after the solid material is deposited in a pond or landfill.

Leachates from ponds or landfills are not the only secondary aqueous emissions which occur. Particles that are emitted to the atmosphere with effluent gases eventually fall to earth, but the trace elements associated with them are not mobilized to the environment unless or until they dissolve in aqueous solution.

TABLE 5-17. AVERAGE CONCENTRATIONS OF TRACE ELEMENTS IN LIQUORS FROM ASH PONDS AT COAL-FIRED POWER PLANTS OPERATED BY THE TENNESSEE VALLEY AUTHORITY (all concentrations in mg/liter)

Element	Plant A Fly Ash Pond	Plant A Bottom Ash Pond	Plant B Fly Ash Pond	Plant B Bottom Ash Pond
Arsenic	0.010	0.006	0.03	0.018
Barium	0.3	0.2	0.1	0.1
Beryllium	0.01	<0.01	<0.01	<0.01
Cadmium	0.037	0.001	0.001	0.003
Chromium	0.067	0.009	0.02	0.01
Copper	0.31	0.065	0.02	0.041
Lead	0.06	0.02	0.01	0.02
Manganese	0.48	0.16	0.13	0.58
Mercury	0.0003	0.0007	0.001	0.001
Nickel	1.1	<0.05	0.05	0.12
Selenium	0.002	0.002	0.015	0.011
Silver	<0.01	<0.01	<0.01	0.01
Zinc	1.51	0.09	0.06	<0.14
pH	4.4	7.2	8.0	9.8
TDS	7.2	167.	142.	524.

SOURCE Chu, *et al*. (45).

TABLE 5-18. AVERAGE CONCENTRATIONS OF TRACE ELEMENTS IN LIQUORS FROM COMBINED ASH PONDS AT COAL-FIRED POWER PLANTS OPERATED BY THE TENNESSEE VALLEY AUTHORITY (all concentrations in mg/liter)

Element	Plant C	Plant D	Plant E	Plant F	Plant G
Arsenic	0.013	0.03	0.005	<0.005	0.029
Barium	0.2	0.2	0.2	0.2	0.2
Beryllium	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium	0.005	0.001	0.001	0.001	<0.001
Chromium	0.005	0.004	0.019	0.043	0.012
Copper	0.03	0.01	0.08	0.02	0.03
Lead	0.02	0.01	0.014	0.01	0.01
Manganese	0.22	0.03	0.01	0.01	0.05
Mercury	0.015	0.0002	0.0002	0.038	0.0008
Nickel	<0.05	0.05	<0.05	<0.05	<0.05
Selenium	0.014	0.065	0.009	0.016	0.010
Silver	0.01	<0.01	<0.01	<0.01	<0.01
Zinc	0.12	0.03	0.05	0.04	0.03
pH	7.1	8.6	11.2	11.2	9.6
TDS	363.	151.	380.	452.	279.

SOURCE: Chu *et al*. (45)

TABLE 5-19. CONCENTRATIONS OF TRACE ELEMENTS IN LIQUORS FROM COMBINED ASH PONDS AT COAL-FIRED POWER PLANTS OPERATED BY THE TENNESSEE VALLEY AUTHORITY (all concentrations in mg/liter)

Element	Plant H	Plant I	Plant J	Plant K	Plant L
Arsenic	0.10	0.005	0.038	0.012	0.036
Barium	0.2	0.2	0.2	0.2	0.1
Beryllium	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium	<0.001	<0.001	0.001	<0.001	0.001
Chromium	0.006	0.024	0.006	0.021	0.008
Copper	0.05	0.05	0.06	0.05	0.04
Lead	0.01	0.01	0.02	0.025	0.01
Manganese	0.05	0.01	0.39	0.01	<0.01
Mercury	0.0006	0.0002	0.0003	0.0004	0.0003
Nickel	0.05	<0.05	0.05	0.07	<0.05
Selenium	0.013	0.004	0.003	0.011	0.010
Silver	< 0.01	<0.01	<0.01	<0.01	<0.01
Zinc	0.04	0.08	0.05	0.05	0.04
pH	8.5	11.3	6.3	10.8	10.5
TDS	268.	270.	197.	232.	219.

SOURCE: Chu _et al_. (45)

The solubility of trace elements in ashes is related to the chemical form of the element in the ash. It is also related to the concentration of the element at the surface of the ash. Several studies have indicated that several trace elements are concentrated on the surfaces of fly ash particles. The subject of surface predominance of trace elements is discussed at length in Section 5.5 of this report. Some references to leaching behavior are contained in that section. However, reports concerned primarily with leaching behavior of fly ashes and related topics are discussed in the current section. Reports from laboratory studies and field studies are included.

Mobilization of trace elements to the environment requires initial solubility in water. Continued solubility after the leachate interacts with natural surface water or with groundwater and soils also is required. Results of field studies and laboratory studies concerned with the interaction of trace elements in solution with hydrous oxides in the solid phase are outlined.

5.4.1 Laboratory Study of Trace Element Emissions from Coal Refuse Pile Leachate

Wewerka et al. (46) have reported the results of a study of trace element contamination of drainage from coal and coal cleaning wastes. Their study was aimed toward cleaning wastes generated at the mine rather than at the point of use. But, some of their results can be adapted to drainage from coal storage piles at the combustion site and refuse piles generated at the combustion site.

This study of Wewerka et al. was concerned only with coals from the Illinois Basin. Coals and associated refuse from other coal producing areas will be the subjects of further studies.

The objectives of the program were to assess the potential for environmental pollution from trace and minor elements released in the drainages from coal preparation wastes and stored coals. Suitable control measures, if necessary, were to be identified. Trace elements were defined as all elements except carbon, hydrogen, sulfur and oxygen. The levels and occurrences of trace elements were determined in refuse samples. Minerals in the coal refuse were identified.

Elements present in major proportions such as iron, aluminum and silicon made up the major minerals identified. Minor elements occurred as constituents of minor minerals, components of residual coal, or as substituents in the major mineral lattices. Several elements which are generally considered to be environmentally sensitive were found in refuse in concentrations above 30 µg/g. Among the elements found in these concentrations were fluorine, aluminum, manganese, iron, cobalt, nickel, copper, zinc, arsenic, and lead.

Static and dynamic leaching studies were carried out. These experiments were needed so quantitative predictions could be made about trace element concentrations in drainage from coal refuse dumps and coal storage piles. The concentration of sulfur was high in the refuse materials studied. These materials had a pronounced tendency to produce acidic leachates rapidly. Leachates from the refuse samples studied were reported typically to have pH values in the range 2 to 4.

The acidic leachates were very efficient in dissolving or degrading many of the mineral components. When the mineral components were dissolved or degraded, trace or minor elements were released.

Two types of trace element leachabilities were observed. Some elements (iron, aluminum, calcium, magnesium) were released in high absolute quantities because they were abundant in the materials being leached. Other less abundant elements (nickel, cobalt, zinc, copper) were found to be highly leachable from the refuse. These elements were present in relatively higher concentrations in the leachates than in the refuse materials.

Studies designed to simulate intermittent leaching showed that intermittently leached dumps presented a greater pollution threat than those wastes that were always in contact with water. If not in contact with water, the $S^=$ oxidized to $SO_4^=$ which is water soluble creating a more acidic solution, thereby activating more trace metals.

Comparisons were made between the results of laboratory leaching studies and leachates taken from refuse dumps. The high level of agreement between the two sets of results was taken to indicate that the laboratory studies realistically simulated refuse dump conditions.

Nine elements were identified as having the greatest potential to contaminante drainage or run-off from Illinois Basin coal preparation wastes. These elements are listed in Table 5-20. The table also gives the reasons these elements were selected as priority elements.

TABLE 5-20. TRACE ELEMENTS OF MOST ENVIRONMENTAL CONCERN IN LEACHATES FROM HIGH-SULFUR ILLINOIS BASIN COAL REFUSE

Elements	Labile Mineral Association	High Leachate Concentration	High Inherent Leachability
Aluminum		X	
Cadmium			X
Cobalt		X	X
Copper		X	X
Fluorine	X		
Iron	X	X	X
Manganese	X	X	X
Nickel		X	X
Zinc		X	X

SOURCE: Wewerka *et al*. (46)

The authors pointed out that almost any designated level of trace elements in a refuse drainage system is somewhat arbitrary from an environmental viewpoint. The actual harm that toxic elements can cause is a function of the accumulation in the surrounding ecosystem. Factors such as the volume and dilution of the drainage and the ability of plants, animals and soils in the area to concentrate specific toxic elements must be considered.

The authors noted that refuse piles from low sulfur, alkaline western coals could be expected to exhibit leaching characteristics very different from those observed for Illinois Basin coals.

Constituents of coal pile run-off, as reported by Hart *et al*., were given previously in Table 5-7.

5.4.2 Trace Element Concentrations in Leachate from Ponded Ash and Sulfur Dioxide Scrubber Sludge

Holland et al. (47) and Carlisle et al. (48) have reported the results of a study regarding possible trace element contamination of groundwater from disposal of solid wastes from coal-fired power plants. Ash and sludge from five operating plants were mixed with water to simulate ponding. Trace element concentrations in the resulting aqueous phase were near the analytical detection limit. Soil leaching tests indicated that soil under a pond could remove trace elements from the leachate.

Concentrations of trace elements in coal ash leachate as reported by Holland et al. are listed in Table 5-21. Station 1 fired low sulfur western coal. Stations 2 and 4 fired eastern coal which contained approximately 4 percent sulfur. Station 3 fired high sulfur eastern coal. Particulate emissions were controlled with electrostatic precipitators at the first four stations. Station 5 fired eastern coal with approximately 5 percent sulfur. Station 5 used ash reinjection to control particulate emissions.

The range of concentrations and the median concentration of trace elements in FGD sludge leachates, as reported by Holland and Jones (39), were listed above in Table 5-8.

Rossoff and Rossi (40) described the chemical composition of leachate from sulfur dioxide scrubber sludge. Values were given for two sludges. One sludge was from a plant burning eastern coal and the other was from a plant burning western coal. The concentrations of trace elements in these leachates also were reported in Table 5-8 above.

Jones et al. (49) have reported the results of a coordinated laboratory study of flue gas cleaning wastes. Flue gas cleaning wastes include coal fly ash, sulfur dioxide scrubber sludge and mixtures of fly ash and sludge. The chemical and physical properties of these materials were investiaged. Trace element concentrations in leachates from selected fly ashes and ash-sludge mixtures were reported to be below EPA drinking water standards in most cases, however, trace element concentrations were above drinking water

TABLE 5-21. EQUILIBRIUM CONCENTRATIONS OF TRACE ELEMENTS IN COAL ASH LEACHATE

	Station Number				
	1	2	3	4	5
Bottom Ash (wt%)	20	20	20	50	100
Precipitator Ash (wt%)	80	80	80	50	—
pH	12.5	9.5	12.2	12.0	8.2
Element μg/g					
Antimony	.006	.018	.033	.022	.0087
Arsenic	<.002	.084	.015	.072	.006
Barium	40	<.3	<.3	<.3	<.3
Beryllium	.003	.00064	.0007	.001	.00026
Boron	.03	16.9	.21	1.1	.048
Cadmium	<.001	.0025	<.01	<.001	.0011
Chromium	<.001	.21	.11	1.0	.014
Copper	<.005	.031	.092	.013	.015
Fluorine	2.3	1.4	2.0	17.3	1.4
Germanium	<.01	<.01	<.01	<.01	<.01
Lead	.0068	.0027	.024	.0043	.0063
Manganese	<.002	<.002	<.002	<.002	<.002
Mercury	.0006	.0005	.015	.0003	.0003
Molybdenum	.047	.052	.05	.69	.010
Nickel	<.05	.015	.025	<.05	.046
Selenium	.009	<.0005	.033	.47	<.0005
Vanadium	<.1	<.1	<.1	<.2	<.1
Zinc	.038	.025	.19	<.005	.0175

Source: Holland et al. (47).

standards in a significant number of cases. The values reported are summarized in Table 5-22.

5.4.3 Sorptive Behavior of Trace Metals on Fly Ash in Aqueous Systems

Theis and Wirth (50) reported the results of chemical extraction of trace elements from the surface of fly ash particles. Ashes collected by electrostatic precipitators from 11 coal-fired power plants were studied. Chemical extractants used were:

- hydrofluoric acid and aqua regia (for complete dissolution),
- ammonium oxalate (to dissolve X-ray amorphous oxides of iron, aluminum and manganese),
- hydroxylamine hydrochloride at pH = 3 (for selective dissolution of manganese oxides), and
- aqueous solutions of sodium hydroxide or perchloric acid (to determine extractabilities of elements in fly ash at pH = 3, 6, 9, and 12).

Relative amounts of lime and amorphous iron oxides were reported to define the acidic or alkaline nature of fly ash in the presence of excess water. The natural pH of water in contact with the ashes studied varied from about 4 to above 12.

Extraction studies have shown that at least seven trace metals tend to associate with the more abundant metal oxides (Fe_2O_3 and MgO). Furthermore, differential extractions were used to estimate the degree of surface concentration (enrichment) of the seven trace elements studied.

The oxides of aluminum, iron, and manganese were presumed to be available on the surfaces of the fly ash particles. Arsenic, chromium, copper and zinc were found to be preferentially extracted with iron for most of the fly ashes studied. Chromium and nickel were found to be preferentially extracted with manganese for most of the fly ashes studied. Lead was preferentially extracted with manganese for five fly ashes and with iron for three fly ashes.

Table 5-23 lists the range of concentrations found for each of the seven trace elements studied for eleven ashes. The mean concentration of each element is given. This table also lists a measure of the surface

TABLE 5-22 CONCENTRATION OF POTENTIAL PROBLEM SPECIES IN SELECTED FLY ASH AND SLUDGE LEACHATES[1]
(all concentrations are in mg/liter)

Element	Artificial Sludge[2,3]						Fly Ash	
	Ash #1	Ash #2	Ash #3	Ash #4	Ash #5	Ash #6	Ash #7	Ash #8
Arsenic	.02	.08[4]	.16	.03	.02	<.003	.01	.01
Barium	.2	1.0	.14	.9	.2	2	1	.2
Boron	.6	.08	.8	.8	.003	.02	.9	.01
Cadmium	<.002	<.002	<.002	.002	<.001	.003	≤.002	≤.001
Chlorine	1140	2820	2440	2	.05	2	.8	.2
Chromium	.02	.4	.02	.07	.002	.02	.03	.02
Copper	.018	.02	.02	.009	.009	.02	.02	.01
Fluorine	≈2	≈.4	≈1.4	≈.2	≈.05	≈.05	≈.5	≈2
Iron	.2	.2	.18	.2	.07	.1	1	.2
Lead	≤.01	≤.009	.045	.005	.003	.01	.06	.009
Manganese	.02	<.001	.004	.003	.02	.001	.01	.009
Selenium	<.007	<.02	<.006	.01	.005	.01	.02	.02
Silver	<.002	<.002	<.002	<.001	<.001	.001	≤.001	<.001
Sulfate	5140	2400	2400	1430	1600	1440	910	1420
Zinc	.4	.04	.06	.02	.01	.02	2	.06
TDS	9640	7750	8090	2310	2290	2450	1560	2690
pH	11.1	10.5	10.0	11.2	7	10.9	9.7	6.5

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[1] Trace element concentrations were estimated by Spark Source Mass Spectroscopy which has an error limit of ± a factor of 2.

[2] The composition of artificial sludge was 50 percent by weight calcium sulfite-sulfate co-precipitate prepared in the laboratory and 50 percent fly ash.

[3] Artificial sludges prepared with Ashes Nos. 1, 2 and 3 were leached using a "worst case" batch leaching test. The other samples were leached using column leaching test.

[4] Concentrations which have been underscored are equal to or exceed water quality standards.

SOURCE: Jones *et al.*, (49)

enrichment of these elements. The measure of surface enrichment is the percentage of the element which was extracted under the conditions used. Ranges and mean values are given for each element.

TABLE 5-23. AVERAGE CONCENTRATIONS AND SURFACE ENRICHMENT OF TRACE ELEMENTS FOR ELEVEN FLY ASHES

Element	Average Concentration (μg/g of Fly Ash) Range	Mean	Surface Enrichment (Percent of Total) Range	Mean
Arsenic	6-1200	157	65-100	93
Cadmiun	5-20	8.1	<2-58	25
Chromium	44-320	109	15-84	44
Copper	28-350	97	25-75	48
Lead	30-1120	157	5-40	8
Nickel	90-600	220	5-42	11
Zinc	100-3300	515	10-70	30

SOURCE: Theis and Wirth (50)

The seven elements studied were leached more efficiently with acidic than with alkaline aqueous solutions. Arsenic and, to some extent, cadmium were observed to exhibit increased solubility at pH 12.

The leaching techniques used in this study were said to provide a measure of the amount of trace element available for environmental release on a short-term basis.

The large ranges observed in fly ash composition and surface enrichment were attributed primarily to the variable geochemical matrix in which the trace elements occur in the coal.

Elemental concentrations were determined using atomic absorption spectrophotometry.

A procedure was applied to distinguish between elemental mercury and ionic mercury. Mercury was observed to occur primarily as the element in four fly ashes and primarily in the ionic form in four fly ashes. Three fly ashes had extremely low concentrations of mercury.

The authors point out the extreme variability of trace element concentrations and mode of occurrence in fly ashes. They caution against using studies of only one fly ash or averages of values determined for several fly ashes to predict effects for a particular situation.

Talbot et al. (51) have reported the results of another study concerning adsorption reactions. They report that adsorption reactions have an important influence over the dissolved concentrations of cadmium and phosphorous in aqueous media in contact with coal fly ash.

5.4.4 Chemical Speciation of Heavy Metals in Power Plant Ash Pond Leachate

Theis (52) has been concerned with properties of ash pond leachate. More recently, Theis and Richter (53) have reported measurements of concentrations of seven trace elements near a power plant ash pond. The power plant was located in an area of sand dunes adjacent to Lake Michigan, and used high sulfur coal from Southern Illinois as fuel. Elemental concentrations of arsenic, cadmium, chromium, copper, lead, nickel and zinc were measured in soil particles and in the associated aqueous phase. The computer model REDEQL2 was used to calculate the chemical species of the trace elements (except arsenic) in the systems studied.

The approach taken by these authors is unique with respect to application to effluents from combustion wastes. This approach makes it possible to estimate the true impact of leachates upon the environment. The validity of the approach depends heavily upon the reliability of the adsorption constants and solubility product constants in the computer program. Good correlations between measured and predicted metal solubilities for five of the six metals studied lend credibility to the results.

The results of this study are site specific; however, they give one set of interactions between leachates and the environment. Additional studies at other sites with different coals and different soils would be required to obtain a general understanding of these interactions. The results of this study are outlined in the following paragraphs.

Less than one percent of any of the elements existed in a soluble form in the soil-water system studied. The major portion of each element was found to be associated with the solid phase in one way or another. The two primary modes of association with the solid phase were assumed to be adsorption on metal oxides and precipitation as discreet phases. The major sorbing sinks for trace elements were assumed to be the oxides of iron, manganese and silicon.

Soil and leachate samples were taken from several points around the pond. The geometry of the sampling points provided a means of determining the effects of changing soil and leachate properties. Samples taken included pond water, leachate after passing through soil but before mixing with natural groundwater and leachate after mixing with groundwater.

The computer model was capable of calculating the relative amounts of various chemical species present in a chemical system. Thermodynamic equilibrium was assumed. The input data required were total concentrations of trace elements and sorbing metal oxides. In addition, the model required input of the chemical composition of the leachate.

The model calculations indicated that free aquo and sulfato complexes were the dominant soluble species in the pond liquor. As the leachate entered the soil environment several chemical reactions occured. Zinc, cadmium and nickel were sorbed from the leachate onto iron oxide and to some extent onto manganese oxide. This sorption was indicated by model calculations before and after the leachate encountered natural groundwater.

The computer model indicated that the solubilities of chromium, copper and lead were controlled by precipitation of sparingly soluble species. Mixture of the leachate with natural groundwater did not influence the solid phase for chromium and copper. Soluble chromium species were in equilibrium with chromium hydroxide [$Cr(OH_3)$]. Soluble copper species were in equilibrium with basic copper carbonate [$Cu_2(OH)_2CO_3$].

The carbonate in natural ground water changed the form in which lead was predicted to precipitate. In the pond leachate soluble lead species were in equilibrium with lead hydroxide [$Pb(OH)_2$]. In pond leachate mixed with natural groundwater soluble lead species were in equilibrium with lead carbonate ($PbCO_3$).

In the study by Theis and Richter, the partitioning of the elements studies between solid and liquid phases was most influenced by pH, p(FeOOH), p(MnO_x) and p($SO_4^=$). In general, higher pH was predicted to result in greater adsorption and precipitation. Chromium was an exception to this generalization. Chromium solubility was predicted to increase at pH values above 7.5 because soluble hydroxo complexes such as $Cr(OH)_4^-$ form. Changes in pH also influenced predictions about which solid phase controlled solubility for lead and copper.

The amount of available surface area of iron oxide or manganese oxide was predicted to influence the amount of trace elements in the liquid phase.

Sulfate concentrations in the leachates studied were not shown to influence solubilities; however, the model predicted that sulfate concentrations above about 0.01 molar (1000 mg/ℓ) could be expected to increase the solubilities of all the trace elements studied except chromium.

5.4.5 Effect of Complexing Ligands on Trace Metal Uptake by Hydrous Oxides

Davis and Leckie (54) have reported the results of a laboratory study concerning the sorptive behavior of trace elements. In this study, silver and copper ions in solution were sorbed onto amorphous iron oxide in suspension. Sorption studies were carried out at several values of pH and with and without complexing ligands present. Inorganic and organic ligands were used.

The authors studied the adsorption behavior of complexing ligands. This behavior must be considered in determining the overall sorption of trace elements on hydrous oxides. In some cases metal sorption was increased in the presence of ligands because the ligands were sorbed on the surface of the oxide. Other ligands were not sorbed but remained in solution and competed with the hydrous oxide surface for coordination of metal ions.

The authors suggested that the distribution of trace elements in natural aqueous systems may not be controlled by simple sorption on hydrous metal oxides. They suggested that trace elements may be bound on the surfaces of colloidal particles coated with humic compounds.

5.5 VARIABLE DISTRIBUTION OF TRACE ELEMENTS BETWEEN BOTTOM ASH AND FLY ASH AND AMONG VARIOUS SIZE FRACTIONS IN FLY ASH

A number of studies have reported enrichment of certain trace elements in precipitator ash relative to bottom ash. Several studies have reported variable concentrations of a number of elements in various size fractions of precipitator ash or fly ash. Some elements have been reported to concentrate in the finest particulates. Other elements have been reported to exhibit concentration maxima or minima as a function of particle size.

The most popular explanation of these phenomena involves volatilization, followed by condensation of the enriched elements on the fine particles. Most authors suggest that the elements which volatilize are those which have elemental boiling points below or near the maximum temperature in the combustion zone (1500-1600°C). Suggestions have been put forth that elements may have access to the vapor phase in various compounds (oxides or carbonyls). Other authors have suggested that elements may have access to the vapor phase because they are associated with organic matter in the coal, or because they are associated with the sulfur bearing minerals in the coal. Some studies have concentrated on demonstrating surface predominance of certain elements.

Some elements are reported to exhibit enrichment in most studies on this subject. Other elements are reported to exhibit one type of behavior by one study and another type by another study. Thus, it appears that a number of variables influence enrichment behavior. The results of several of the studies in this area are summarized briefly in the following sections.

5.5.1 Enrichment of Trace Elements as a Function of Particle Size in Aerosols Leaving an Electrostatic Precipitator and a Wet Scrubber

Ondov *et al*. (1) reported enrichment of some elements with particles emitted from wet scrubbers relative to particles emitted from an electrostatic precipitator at the same power plant. (This plant was described in Section 5.1.1 of this report). Elements reported to be enriched in this way included: antimony, arsenic, bromine, chromium, selenium, uranium, and vanadium.

The scrubber aerosols were reported to contain a greater proportion of their mass in particles of respirable sizes. The authors concluded that wet scrubbers were less effective in reducing the potential inhalation hazard from particulate emissions than were electrostatic precipitators of comparable efficiencies.

Mass median aerodynamic diameters of particles associated with several elements leaving a scrubber and an electrostatic precipitator are given in Table 5-24.

5.5.2 Characterization of Trace Element Emissions from Coal-Fired Power Plants

Ondov et al. (55) have reported enrichment factors for elements in aerosols from five coal-fired plants. They had measured elemental concentrations in particles from two of the plants. The enrichment factors were calculated from their measurements and from reports of others. The enrichment factors are presented in Table 5-25.

These same authors [Ondov et al. (56)] have reported the results of an earlier study of trace element distribution in particles sized with an inertial cascade impactor. These authors also have collaborated with others [Ondov et al. (57)] to report time-phased measurements of elemental concentrations in the plume and in the stack of a western coal-fired power plant.

5.5.3 Trace Element Partitioning in the T.A. Allen Steam Plant

The T.A. Allen Steam Plant was described in Section 5.1.2 of this report. Lyon (2) reported partitioning of elements between the gas phase, fly ash leaving the electrostatic precipitator, precipitator ash, and bottom slag. Three types of partitioning behavior were observed. The various elements were assigned to classes based on their partitioning behavior. Enrichment factors for this plant were presented in Table 5-25.

Class III elements were those that remained essentially completely in the gas phase. Bromine, chlorine and mercury were reported to belong to this class.

TABLE 5-24 MASS MEDIAN AERODYNAMIC DIAMETERS (MMAD) OF ELEMENTS IN AEROSOLS EMITTED FROM TWO COAL-FIRED ELECTRICAL GENERATING UNITS

ESP unit, July 1975		Scrubber units, Feb. 1976	
Elements	MMAD[1] (μm)	Elements	MMAD[1] (μm)
Cr, Cs, Rb, Zr	10.7-12.3	Co, Cr, Ni	7.1-12
		Fe, K, Mg, Na, Zn	3.0-4.0
Al, Br, Ce, Co, Dy Eu, Fe, Hf, K, La Lu, Mg, Nd, Sc, Sm, Ta, Tb, Th, Ti	9.1-10.0	Al, Br, Ce, Dy, Eu Hf, Lu, Sc, Sm, Th, La	1.4-2.1
		Ca, Ga, In, Mo	1.69-0.81
Ca, Mn, Na, Se	7.9-8.6		
As, Ba, Ga, In Mo, Sb, U, V, W, Zn	4.4-6.3	As, Ba, Sb, Se, U, V, W,	0.49-0.59

[1] Range of median values of MMADs from distributions of up to 6 impactor samples.

SOURCE: Ondov, _et_ _al_. (1)

TABLE 5-25 ENRICHMENT FACTORS FOR ELEMENTS IN AEROSOLS EMITTED FROM SEVERAL COAL-FIRED POWER PLANTS

	Ondov Plant A	Ondov Plant B	Lyon[1]	Gladney[2]	Kaakinen[3]
Aluminum	0.86	0.75	0.44	0.83	0.94
Antimony	7.0	5.3	6.7	4.0	--
Arsenic	6.6	7.9	6	6.3	--
Barium	2.5	2.7	0.7	0.92	--
Beryllium	--	0.6	--	0.64[4]	--
Bromine	0.2	0.1	--	0.17	--
Cadmium	--	6.0	--	--	--
Calcium	0.76	0.89	--	0.92	--
Chromium	2.5	2.6	3.0	1.1	--
Cobalt	2.3	1.7	1.4	1.0	--
Gallium	4.3	3.0	--	1.2	--
Indium	5.5	3.7	--	--	--
Iron	1.1	0.90	0.84	0.83	1.0
Lead	--	3.8	8.1	3.7	3.1
Magnesium	1.1	0.8	0.54	--	--
Manganese	0.68	1.1	0.78	--	--
Molybdenum	1.8	3.5	--	--	3.0
Potassium	1.0	0.7	0.95	0.83	--
Scandium	1.0	1.0	1.0	1.0	--
Selenium	3.0	5.3	5.5	5.7	1.7
Sodium	1.0	1.1	0.99	--	--
Thorium	0.95	0.90	0.76	--	--
Tungsten	--	4.9	--	--	--
Uranium	3.3	2.5	--	--	--
Vanadium	2.0	2.5	2.5	0.75	--
Zinc	4.3	4.3	7.8	1.5	2.5

---

[1] Based on data of Klein *et al*. (6).

[2] Unless indicated, values are based on data of Gladney *et al*. (24) and Gordon *et al*. (58).

[3] Derived from data of Kaakinen *et al*. (19) for the ESP-equipped unit. Data normalized to Fe. The value for Pb was based on ^{210}Pb.

[4] Based on value from Gladney and Owens (25) normalized to Sc.

SOURCE: Ondov *et al*. (55)

Eight elements were reported to be in Class II. These elements are poorly incorporated into slag and exhibited successive enrichment in inlet fly ash and outlet fly ash. The elements belonging to this class were:

antimony
arsenic
cadmium
copper
gallium
lead
selenium
zinc.

Twenty-five elements were reported to belong to Class I. These elements were readily incorporated into the slag and showed no definite tendency to concentrate in the smaller particles. They were:

aluminum
barium
calcium
cerium
cesium
chromium
cobalt
europium
hafmium
iron
lanthanum
magnesium
manganese
potassium
niobium
scandium
silicon
samarium
sodium
strontium
tantalum
thorium
titanium
uranium
vanadium.

Two elements, nickel and molybdenum, did not fit the classification scheme outlined above. Lyons stated that molybdenum probably should be included in Class II and nickel probably should be assigned to Class I.

5.5.4 Trace Element Partitioning in Atmospheric Emissions from Plants Using Hot-Side and Cold-Side Electrostatic Precipitators

Two western coal-fired power plants were described in Section 5.1.3 of this report. One plant used a hot-side electrostatic precipitator for particulate control. The other plant used a cold-side electrostatic precipitator for particulate control. Mann et al. (3) reported that the aims of the study were to:

- quantify trace element enrichment in fly ash compared to raw coal,
- determine trace element enrichment as a function of particle size,
- investigate the affinity of elements for inorganic or organic fractions of coal, and

- investigate particulate collection efficiency and trace element enrichment of emitted fly ash of hot-side and cold-side electrostatic precipitation control devices.

Trace elements in coals may be associated with the inorganic (mineral) portion of the coal or with the organic portion of the coal. Coal from each of the plants studied was separated into four density fractions (<1.35, >1.35; and <1.45, >1.45) using a sink-float technique. Each of the fractions was analyzed for 15 trace elements. The organic-inorganic association of each element was calculated.

Correlation of enrichment of certain trace elements with decreasing particle size in the fly ash was investigated. Good correlation of increasing enrichment with decreasing particle size was found for four elements (arsenic, copper, nickel, zinc) for both plants.

Three additional elements exhibited this correlation only at the cold-side station: cadmium, chromium, and manganese. Selenium also exhibited a good correlation of enrichment with decreasing particle size but only at the hot-side station.

Enrichment of volatile trace elements in the fly ash leaving the control devices was said to depend on two factors. These factors were:

- particulate loading at the point of condensation, and
- degree of element volatilization.

Particulate loading at the point of condensation was said to determine the available surface upon which condensation could occur. A high particulate loading was reported to lead to lower enrichment than a low particulate loading. The surface area available for condensation would be greater with the higher loading. The location of condensation with the process will vary from element to element and will depend on the temperature profile of the gas stream.

The higher enrichment of arsenic and selenium in particles leaving the hot-side electrostatic precipitator was attributed to condensation of these elements in the air preheater. The particulate loading in the air preheater would be much lower in a plant with a hot-side electrostatic precipitator than in a plant with a cold-side electrostatic precipitator.

The degree of elemental volatilization was reported to depend on the characteristics of the element and its association in the coal.

An element such as mercury with a low boiling point is volatilized at fairly low temperatures. Other elements such as iron or nickel are susceptible to forming volatile metal carbonyls in gas streams rich in carbon monoxide. Arsenic, cadmium, chromium, lead, nickel, selenium and zinc exhibit boiling points either as the element or as a compound which would result in partial volatilization in the boiler.

Kuhn and Shimp (59) have reported that the association of an element with the organic fraction of coal influences the volatility of that element during pyrolysis or combustion. Several elements were observed by Mann et al. to be preferentially associated with the organic phase in the coal. These elements also exhibited higher enrichment in the fly ash from the station with the cold-side electrostatic precipitator. Elements exhibiting this behavior were:

- beryllium
- cadmium
- chromium
- copper
- fluorine
- mercury
- uranium
- zinc.

Mann et al. pointed out that although a relationship of enrichment with organic phase association was found, a larger data base was needed to establish a valid correlation.

5.5.5 Trace Element Enrichment in Vapors and Particles Emitted to the Atmosphere from Three Western Power Plants

Three western coal-fired power plants were described in Section 5.1.4 of this report. Radian Corporation (4) reported that 18 elements were concentrated in the flue gas stream and depleted in the bottom ash stream of Station I. The flue gas stream included entrained particles. Elements which exhibited this behavior were:

antimony
arsenic
boron
cadmium
chlorine
chromium
cobalt
copper
fluorine
lead
mercury
molybdenum
nickel
selenium
silver
sulfur
vanadium
zinc.

Eight elements were distributed in proportion to total ash flows in Station I with no significant concentration or depletion. These elements are listed below:

aluminum
barium
beryllium
calcium
iron
magnesium
manganese
titanium.

Uranium was concentrated in the bottom ash and depleted in the precipitator ash of Station I.

Thirteen elements were observed to be enriched in the flue gas (and entrained particles) of Station II. These elements were:

antimony
boron
cadmium
chlorine
chromium
fluorine
lead
mercury
molybdenum
nickel
selenium
sulfur
zinc.

Five elements were found to be enriched in the precipitator ash stream of Station II. These elements were:

arsenic
cobalt
copper
silver
uranium.

Nine elements were found to be uniformly distributed in the ash stream of Station II. These elements were:

aluminum
barium
beryllium
calcium
iron
magnesium
manganese
titanium
vanadium.

Fifteen elements were found to be enriched in the flue gas stream of Station III (including entrained particles).

antimony
boron
cadmium
chlorine
chromium
cobalt
copper
fluorine
lead
mercury
molybdenum
nickel
selenium
sulfur
zinc.

Three elements, arsenic, silver, and uranium, were enriched in the cyclone plus economizer ash for Station III.

Nine elements were found to be distributed in proportion to the amount of ash present in Station III. These elements were:

aluminum
barium
beryllium
calcium
iron
magnesium
manganese
titanium
vanadium.

In addition to the results presented above, enrichments of some elements in fly ashes as determined by spark source mass spectrometry (SSMS) were reported for all three stations. This report contains quantitative information concerning degree of enrichment of each element for each station studied.

5.5.6 Trace Element Partitioning in Effluent Particles from the Widows Creek Power Plant

The Widows Creek Power Plant was described in Section 5.1.4 of this report. Cowherd *et al*. (5) reported that chromium and lead were enriched in outlet fly ash compared to coal ash.

Measurements of concentrations of 15 elements in samples collected in a Brink particle size train were presented. The authors reported that the values were subject to error since large blanks had to be subtracted from the reported values. The reported values indicate successive enrichment in smaller particles for many of the elements measured. Other elements exhibited apparent maximum concentrations at intermediate particle sizes. Elements exhibiting successive enrichment were:

beryllium
cadmium
copper
manganese
thallium
vanadium
calcium.

The following elements had a maximum concentration at 0.56 to 0.87 μm equivalent diameter:

chromium
cobalt
lead
tin
zinc.

Nickel exhibited a maximum concentration at 0.87 to 1.51 μm equivalent diameter and iron a maximum concentration at 1.6 to 2.35 μm.

5.5.7 Enrichment of Trace Elements in Particulate Emissions from the Chalk Point Electric Generating Station

The Chalk Point Electric Generating Station was described in Section 5.2.2 of this report. Gladney *et al*. (24) reported enrichment factors relative to Chalk Point coal for the precipitator ash, and for ash collected from the effluent gases.

Enrichment factors plotted as a function of particle size exhibited three types of behavior. One group of trace elements (antimony, arsenic, and lead) showed a definite increase in enrichment factor on small particles.

Another group of trace elements (bromine, iodine, mercury and selenium) were observed to exhibit enriched concentrations in the smallest particles, have a minimum in enrichment in particles around 1 μm in diameter and to exhibit another enrichment factor maximum in large particles. No explanation was offered for this bimodal distribution.

Most elements measured exhibited little enrichment factor dependence as a function of particle size. Elements in this group were:

chromium
gallium
nickel
sodium
zinc.

Other elements which exhibited little enrichment factor structure, or whose distributions were not shown were:

barium
calcium
cobalt
hafnium
manganese
magnesium
potassium
all rare earths except cesium
rubidium
scandium
strontium
tantalum
titanium
thorium
vanadium, and
zirconium.

Iron and cesium were reported to be depleted in small particles and enriched in large particles. The authors suggested that the iron distribution might be explained by noting that the iron in the coal occurs primarily as pyrites. They suggested further that pyrites might be expected to behave differently from aluminosilicates during combustion. No explanation was offered for the observed behavior of cesium.

5.5.8 Enrichment of Trace Elements in Particulate Matter Associated with the Valmont Power Plant

The Valmont Power Plant was described in Section 5.2.1 of this report. Kaakinen *et al*. (19) found six elements were enriched in the particles leaving with the effluent gases from the precipitator outlet and scrubber outlet. These elements were:

antimony
arsenic
copper
lead
molybdenum
zinc.

These elements were referred to as "Group B." The authors noted that all oxides of Group B elements, except copper, volatilize completely at temperatures below 1500°C. The boiling point of Cu_2O is 1800°C. These elements are classified geochemically with sulfur bearing minerals in the earth's crust (chalcophile).

Elements found to show no pronounced enrichment were:

iron
niobium
rubidium
strontium
yttrium.

These elements were referred to as "Group A." These elements (except rubidium) have oxide boiling points greater than 2400°C. The author hypothesized that rubidium was associated with the aluminosilicate portion of the ash and did not volatilize. Group A elements are classified geochemically as lithophile.

Zirconium was depleted in the particles leaving with the flue gases. The authors reported that zirconium often occurs in coal as zircon which has a melting point of 2550°C. They suggested that zircon would not melt in the furnace to form glassy spheres and that the mineral would occur in relatively large particles and therefore would be collected by the mechanical collectors more efficiently than the bulk of the fly ash.

5.5.9 Enrichment of Trace Elements on the Surface of Particulates Emitted to the Atmosphere from Coal-Fired Power Plants

Natusch and co-workers have carried out a series of experimental studies concerned with enrichment of trace elements in small particles. Two reports of these studies are discussed in this section and two others are discussed in the following section.

Natusch et al. (60) reported that a number of potentially toxic trace elements were concentrated in the smallest particles emitted from coal-fired power plants. The elements they found to be enriched in small particles were: arsenic, antimony, cadmium, lead, selenium, and thallium. They suggested that these elements or their compounds were volatilized during combustion. They suggested further that as the effluent gases cooled, the volatilized elements preferentially adsorbed or condensed onto small particles. They pointed out that small particles pass through conventional control equipment more readily than larger particles.

Precipitator ash and airborne ash which passed through the precipitation system was collected from eight power plants. Precipitator ash was divided into several size fractions. Fractionations were carried out mechanically by sieving and aerodynamically using a Roller particle size analyzer. Airborne fly ash leaving the plant was collected and sized in-situ using an Andersen cascade impactor. Data were reported for only one plant.

Davison et al. (61) presented additional data and an extended interpretation of the data which had been presented by Natusch et al. (60). The fly ashes studied were from a coal-fired power plant burning coal from southern Indiana. Cyclonic precipitators were used to control particulate emissions. The authors presented no information concerning plant characteristics or efficiency of the control system. No gas flow rates or concentrations of particles in the effluent gases were given so no emissions can be calculated. No material balances were attempted.

Davison et al. stated that the trace element content of the ash from the plant studied had been shown to be representative of that in eight U.S. power plants using a variety of coal types.

A variety of analytical techniques were used to measure the concentrations of 25 elements in the fly ashes. The analytical methods used were: spark source mass spectrometry, optical emission spectrography, atomic absorption spectroscopy, and X-ray fluorescence spectroscopy. Data were reported for the method considered most reliable for the element in question.

The following 10 elements were reported to show marked increases in concentration with decreasing particle size:

antimony
arsenic
cadmium
chromium
lead
nickel
selenium
sulfur
thallium
zinc.

These elements exhibited concentration increases well above experimental error. The concentration increases were confirmed by at least two analytical techniques. The increases were consistently observed in a range of samples and were present in the airborne fly ash collected from the ducting.

Eight elements showed limited concentration trends. Concentration trends were found only for the ash collected in the precipitator, or they exhibited non-uniform concentration dependence on particle size. These elements were:

aluminum
beryllium
carbon
iron
magnesium
manganese
silicon
vanadium.

The remaining seven elements showed no concentration trends. They were:

bismuth
calcium
cobalt
copper
potassium
tin
titanium.

The authors presented a model for concentration dependence which involved vaporization of the element or one of its compounds in the combustion zone. Vaporization was followed by condensation or adsorption onto entrained particles. They rejected the hypothesis that the ashing characteristics of pyritic inclusions gave rise to predominantly small particles. They pointed out that at 25°C as much as 80 μg/m of selenium (as selenium dioxide) and 70 μg/m of arsenic (as arsenic trioxide) could exist in the vapor form.

5.5.10 Enrichment of Trace Elements in Coal Fly Ashes Fractionated According to Size, Density and Ferromagnetism; Surface Predominance of Some Trace Elements

Natusch *et al*. (62) separated coal fly ashes on the basis of particle size, particle density and ferromagnetic character. Thirty-two fractions were obtained. Trace element concentrations were measured in each of these fractions.

Common factor analysis and cluster analysis were used to interpret the data. The authors interpreted the correlations identified in terms of particle size, matrix composition of the particles, and the nature of the chemical elements themselves. They suggested:

- The distribution of elements not volatilized during the combustion process depends on the chemical species in which the element exists and the composition of the fly ash matrix;
- The distribution of elements volatilized in the combustion process depends on the composition of the fly ash particle on which the element deposits and the surface area of those particles;
- The distribution behavior of elements partially volatilized is intermediate between that exhibited by the two classes above.

The environmental significance of the above interpretation was said to be three-fold.

- Many potentially toxic elements are preferentially associated with aerodynamically small particles (<1 μm). These particles are preferentially emitted from power plants, have long atmospheric residence times and can deposit in the innermost region of the lung.
- Surface concentration of potassium and sodium on small particles can be expected to lower the electrical resistivity of these particles. This lowered resistivity will make these particles easier to collect in electrostatic precipitators.
- The complex dependence of elemental distributions upon particle matrix composition and particle size suggests that distributions may be very sensitive to coal type and combustion conditions. Translation of distribution information from one fly ash to another should be approached with caution.

Direct evidence of surface predominance was sought by ion microprobe mass spectrometry, Auger microprobe spectroscopy and electron microprobe X-ray spectrometry. Table 5-26 gives the results of the direct determination of surface enrichment of elements on fly ash particles.

Natusch _et_ _al_. (62) also presented preliminary results of extraction experiments.

Linton _et_ _al_. (63) presented additional depth profiles obtained by using the ion microprobe. They presented profiles for leached and unleached fly ash samples. Lead and thallium exhibited the highest relative surface concentrations of the elements leached. Water and dimethylsulfoxide (DMSO) were used as leaching agents.

The results of the leaching experiments are listed in Table 5-27. More than five percent of the iron, lithium, manganese, potassium, sulfur, and thallium present in the ash was dissolved in water under the conditions used. The authors identified four groups of elements based on leachability, the extent of surface predominance, and the effect of leaching on the extent of surface predominance. These groups are summarized in Table 5-28.

5.5.11 Trace Element Concentrations as a Function of Particle Size for Precipitator Ash

Campbell _et_ _al_. (64) have reported major, minor and trace element concentrations as a function of particle sizes in precipitator ash. The ash studied was collected in the electrostatic precipitator of a western coal-fired steam plant. No description of the plant was provided. This ash was separated into 9 size fractions ranging from 0.5 to 50 μm (mass median diameter). Separation was effected using a Bahco Microparticle Classifier and an air elutriation apparatus. This procedure was reported to produce individual size fractions strongly centered about the mass median diameter.

The size fractions were analyzed for 32 elements. Two or three analytical techniques were used for 18 of these elements. Intercomparison of analytical techniques yielded good results in most cases. In some cases

TABLE 5-26 SURFACE PREDOMINANCE OF ELEMENTS IN FLY ASH PARTICLES

Element	Bulk Concentration[1] (μg/g)	Ratio of signal intensity at surface to signal intensity at 500 A° Depth	Technique[2]
Aluminum	>> 15,500	1.1	1, 2, 3
Beryllium	32	6.0	1
Carbon	-	3.5	1, 2
Calcium	> 28,600	1.6[3]	1, 2, 3
Chromium	380	3.3	1, 3
Iron	92,400	0.7	1, 2, 3
Lead	620	11.0	1, 3
Lithium	200	3.8	1
Magnesium	12,300	0.9	1
Manganese	310	6.4	1
Phosphorous	600	3.8	1, 3
Potassium	38,800	7.6	1, 2, 3
Silicon	110,000	1.1	1, 2, 3
Sodium	> 19,700	15.2	1, 2, 3
Sulfur	7,100	7.7	1, 2, 3
Titanium	4,740	0.9	1
Thallium	28	10.0	1
Vanadium	380	2.0	1
Zinc	1,250	7.2	1, 3

[1] Determined by spark source mass spectrometry.

[2] Technique (1) was secondary ion mass spectrometry. Technique (2) was auger electron spectrometry. Technique (3) was electron induced x-ray spectrometry.

[3] Samples derived from only some sources exhibited surface predominance.

SOURCE: Natusch *et al*.(62).

TABLE 5-27 LEACHING OF FLY ASH

Element	Concentration (ppm by wt) in unleached particles	Amount % Leached (wt%)	
		DMSO	H_2O
Calcium	>12000[1]	<1.3	<5.8
Chromium	380	2.4	4.5
Iron	92000	0.7	5.8
Lead	620	3.4	0.4
Lithium	200	17	14
Magnesium	12000	0.6	2.7
Manganese	310	7.1	35
Potassium	39000	0.2	6.0
Silicon	120000	0.1	0.3
Sodium	>53001	<5.2	
Sulfur	7100	27	36
Thallium	30	25	11
Titanium	4700	1.5	0.5
Vanadium	380	1.5	3.9

[1] Could not be quantified. Interferences were present, or analytical lines were too intense to fall within the working range for the internal standards.

SOURCE: Linton *et al*. (63).

TABLE 5-28 SUMMARY OF ANALYTICAL RESULTS - SURFACE CHARACTERIZATION OF FLY ASH PARTICLES

Group	Elements	Significant Surface Peak Observed?	Effect of leaching on concentration in the immediate surface region	Leachibility
A	aluminum silicon titanium	no	insignificant	low
B	iron lithium potassium sodium sulfur	yes	insignificant	moderate to high
C	chromium lead manganese thallium vanadium	yes	depletions observed following leaching	moderate to high
D	calcium magnesium	no	generally not significant	moderate

Source Linton *et al.*, (63).

two analytical techniques gave different values for concentrations but yielded the same type of concentration vs particle size curve. Trace element concentrations in the coal were not given.

The authors identified several groups of elements. In one group the concentration of the element was observed to increase as particle size decreased. The following elements belonged to this group:

arsenic
gallium
lead
magnesium
titanium.

Calcium and strontium belonged to a group that exhibited a concentration maximum in particles of about 5 μm diameter.

The concentration of silicon was observed to increase as particle size increased.

Iron exhibited a concentration minimum in particles of about 15 μm diameter.

The rare earth elements exhibited a concentration maximum at 5 μm and another small one at about 15 μm.

Composition-particle size relationships were measured for other elements but these elements were not assigned to groups by the authors.

5.5.12 Trace Element Emissions from a Coal-Fired Home Heating System and a University Heating System

Block and Dams (65) have reported concentrations of trace elements in ashes from a boiler providing heat for the University of Gent and from a coal-fired home furnace. Elemental concentrations were determined on fly ash fractions collected on Teflon or polyethylene impaction surfaces in an Andersen cascade impactor. The capacity of the home furnace was 14 kg coal per 24 hours and the capacity of the university heating facility was 14 metric tons of coal per 24 hours for each boiler. Anthracite-type coal from Belgian mines was used in both facilities. The coal was crushed to 12 to 24 mm diameter chunks.

Elemental concentrations vs particle size curves were presented for several elements. Elements were placed into three groups according to their elemental mass-size functions. Most of the mass of elements in Group II were emitted in particles with a diameter of less than 1 μm. The mass median diameters for these elements were reported to vary from 0.4 to 1 μm.

The elements in this group were chalcophiles:

antimony
arsenic
copper
indium
mercury
selenium
zinc,

and halogens:

bromine
chlorine
iodine.

The authors assumed that these elements were associated with the organic fraction. These elements were reported to be in higher concentrations in coal relative to crustal rock. The concentrations of these elements were very high in small particles. The concentrations of the chalcophiles also were high in particles of 10 μm diameter emitted from the home heating system. The concentrations of the halogens also were high in large particles emitted from both systems. The concentration minima for halogens occurred at about 3 or 4 μm for fly ash from the home heating system and at about 1 μm for fly ash from the university heating system.

No clear preference for larger or small particles could be established for elements from Group III. Elements which were assigned to this group included:

cadmium
cesium
gallium
gold
manganese
molybdenum
nickel
potassium
sodium
tungsten
vanadium.

Mass median diameters for elements from Group III were reported to vary from 0.8 to 6.2 μm. Concentrations *vs* particle size curves for fly ash from the university heating facility showed pronounced concentration minima for manganese, potassium, sodium and vanadium. The minima were in the 0.6 to 1 μm range.

Elements assigned to Group I were lithophile elements presumed to be associated with the rocky portions of the coal. These elements were:

aluminum
barium
calcium
chromium
cobalt
hafnium
iron
magnesium
rare earth elements
scandium
thorium.

These elements were said to be preferentially associated with the large particles in fly ash. The mass median diameters for these elements were said to vary from 6.3 to 10 μm. Concentrations of these elements were lowest in small particles and highest in large particles. Aluminum, cesium, cobalt, iron and magnesium appeared to have a minimum concentration at about 0.4 μm in fly ash from the home heating system. Aluminum, cesium, cobalt and magnesium appeared to have a minimum concentration in particles of 0.4 to 0.6 μm diameter in the fly ash from the university heating facility.

5.6 EMISSIONS FROM COMBUSTION OF OIL AND GAS

No information was identified relating to trace element concentrations in natural gas. And no data were found for trace element emissions resulting from combustion of natural gas.

Data concerning trace element emissions from combustion of oil in stationary sources was meager compared to data on emissions from combustion of coal. Reports containing relevant data are summarized below.

5.6.1 Environmental Assessment of Oil-Firing in a Controlled Industrial Boiler

Leavitt *et al*. (66) have reported emissions from a 10 MW equivalent boiler. The boiler was capable of burning oil or coal or both simultaneously. The boiler was equipped with a pilot-scale, double-alkali flue gas desulfurization (FGD) unit designed to treat about 30 percent of the total flue gas. Tests were run using coal as the fuel and using oil as the fuel. The FGD unit actually processed an average of 25 percent of the flue gas during the oil-fired tests.

The authors reported that the overall particle removal efficiency of the scrubber was approximately 75 percent for particles generated when oil was the fuel.

Concentrations of 22 trace elements were measured. The concentrations of 11 of these elements exceeded their minimum acute toxicity effluent (MATE) values at the scrubber inlet. The concentrations of 5 of the elements exceeded their MATE values at the scrubber outlet. These 5 elements were: arsenic, cadmium, chromium, nickel and vanadium. Arsenic, cadmium, nickel and vanadium were removed from the gas stream with lower efficiencies than the overall average removal efficiency.

Beryllium emissions were reported to be 0.001 mg/m^3 after scrubbing. This corresponds to half the MATE value for this element. At this concentration, the National Standard for Hazardous Air Pollutants limitation of 10 grams of beryllium per day would be exceeded by boilers of 100 MW or greater capacity.

Mass balances were attempted for 19 trace elements. Mass balance closure was between 50 and 136 percent for 10 of these trace elements. The balances for the remaining elements failed to close within these limits. The authors attributed poor balance closure to the extremely low concentrations of trace elements present and/or contamination of the scrubber recycle solution with materials from the coal-firing tests.

The scrubber cake produced when oil was the fuel contained about 1 percent oil fly ash. The concentrations of all trace elements measured in the scrubber cake except antimony, boron, molybdenum and zinc were above health based MATE values. The concentrations of all trace elements measured in the scrubber cake were above ecology based MATE values. The authors said that specially designed landfills would be required for disposal of scrubber cake. They based this conclusion on the possibility of trace elements leaching from the cake. No leachate data were presented.

Table 5-29 gives trace element concentrations in the fuel oil. Table 5-30 gives trace element emissions in the flue gas before and after the scrubber. Table 5-31 lists the trace element concentrations in the scrubber cake. Trace element emissions in the combined aqueous effluent from the boiler were reported to fall within acceptable limits.

5.6.2 Influence of Heavy Fuel Oil Composition and Boiler Combustion Conditions on Particulate Emissions

Goldstein and Siegmund (70) reported particulate emissions from conventional high sulfur residual fuel oil derived from Venezuelan crude. They also reported particulate emissions from medium sulfur and low sulfur fuel oil. The composition of the particle matter from the high sulfur fuel oil was reported. The composition of the high sulfur fuel oil is given in Table 5-32. Table 5-33 gives the composition of particles collected from a small package boiler burning high sulfur fuel oil.

The authors attributed the failure of carbon and ash values to add up to 100 percent to the decomposition of carbonates, nitrates and less stable sulfates.

5.6.3 Other Studies of Emissions from Oil-Fired Facilities

Bennett and Knapp (71) reported trace element concentrations of particles collected from three oil-fired power plants. Two of the plants burned high sulfur (2.5 percent) fuel oil and one burned low sulfur (1.4 percent) fuel oil. The major components of the particles were reported to be sulfur, vanadium and nickel.

TABLE 5-29 CONCENTRATION OF MAJOR TRACE ELEMENTS IN OIL

Element	Concentration in Fuel Oil(μg/g)	Typical Range	Reference
Aluminum	3.5	No Data	
Antimony	0.03[2]	0.002-0.8	6
Arsenic	2.0[3]	0.0006.1.1	6
Beryllium	<0.05[4]	No Data	
Boron	<0.15	No Data	
Cadmium	<3.5	No Data	
Calcium	5.50	No Data	
Chromium	2.2	0.002-0.02	6
Cobalt	<1.25	No Data	
Copper	1.40	No Data	
Iron	12.3	0.003-14	6,7
Lead	2.6[2]	No Data	
Magnesium	<0.4	No Data	
Manganese	0.4[2]	0.001-6	6
Mercury	0.09[5]	0.02-30	
Molybdenum	2.9[2]	<0.1-1.5	6
Nickel	16.0	14-68	8
Selenium	0.7[2]	0.03-1	
Strontium	0.23	No Data	
Vanadium	36.5	15-590	8
Zinc	3.0	No Data	
Zirconium	<0.05	No Data	

[1] Except for V and Ni, these ranges are for U.S. and foreign crude oils, Ranges of V and Ni concentrations are for fuel oils.

[2] Values were calculated from concentrations at the scrubber inlet when inductively coupled plasma optical emission spectroscopy (ICPOES) analysis provided upper limit data only

[3] Arsenic concentration calculated from concentration at the scrubber inlet because ICPOES value appeared to be unreasonably high

[4] Performed by spark source mass spectrometry on a feed oil sample from another test.

[5] Performed by cold vapor analysis on a feed oil sample from another test.

6 Magee _et al_. (67) 7. Woodle & Chandler (68) 8. Bennett and Knapp (69)

SOURCE: Leavitt _et al_. (66)

TABLE 5-30 EMISSION FACTORS AND MASS EMISSION RATES OF TRACE ELEMENTS DURING OIL-FIRING TEST

Element	Emission Factor ng/J		Emission Rate, g/hr		Removal Efficiency %	Enrichment Factor
	Scrubber Inlet	Scrubber Outlet	Scrubber Inlet	Scrubber Outlet		
Aluminum	1.9	0.15	220	18	92	1.0
Antimony	0.02	0.0019	2.5	0.23	91	1.15
Arsenic	0.049	0.0094	5.9	1.1	81	2.37
Beryllium[1]	<0.0003	0.0003	<0.04	0.04	Unknown	>11.9
Boron	0.17	0.012	21	1.5	93	0.87
Cadmium	0.091	0.021	11	2.5	77	2.80
Calcium	0.13	0.022	16	2.7	83	2.03
Chromium	0.055	0.0057	6.7	0.69	90	1.26
Cobalt	0.033	0.0038	3.9	0.46	89	1.43
Copper	0.18	0.002	21	0.27	99	0.15
Iron	1.6	0.088	190	11	95	0.69
Lead	0.065	0.0041	7.9	0.50	94	0.77
Magnesium	0.10	0.0094	12	1.1	91	1.15
Manganese	0.010	0.0013	1.2	0.15	87	1.58
Mercury[2]	0.0006	0.0001	0.05	0.006	87	1.48
Molybdenum	0.072	0.0079	8.7	0.95	89	1.35
Nickel	0.36	0.063	43	7.7	83	2.16
Selenium	0.016	0.002	2.0	0.23	87	1.43
Strontium	0.014	0.0003	1.7	0.038	98	0.28
Vanadium	0.88	0.26	110	31	71	3.61
Zinc	0.20	0.02	24	2.5	90	1.27
Zirconium	0.0049	0.0003	0.59	0.038	94	0.79
Total	6.0	0.78	710	96	87	

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[1] Beryllium was determined by spark source mass spectrometry. The other elements except mercury, were determined by inductively coupled plasma optical emission spectroscopy.

[2] Mercury was determined by cold vapor analysis of SASS train samples taken during another test.

SOURCE: Leavitt, *et al*. (66)

TABLE 5-31 INORGANIC CONTENT OF SCRUBBER CAKE FROM OIL FIRING (DRY BASIS)

Element	Concentration µg/g	MATE[1] Value, µg/g		Degree of Hazard	
		Health	Ecology	Health	Ecology
Aluminum	1,684	160	2.0	11	842
Antimony	3 [2]	15	0.4	0.2	7.5
Arsenic	15 [2]	0.5	0.1	30	150
Boron	40	93	50	0.4	0.8
Cadmium	1 [2]	0.1	0.002	10	500
Calcium	200,000	480	32	417	6,250
Chromium	15	0.5	0.5	30	30
Cobalt	19 [2]	1.5	0.5	13	38
Copper	16	10	0.1	2	160
Iron	2,164	3.0	0.5	721	4,328
Lead	6 [2]	0.5	0.1	12	60
Magnesium	3,799	180	174	21	22
Manganese	6	0.5	0.2	32	80
Molybdenum	14 [2]	150	14	0.1	1
Nickel	132	0.45	0.02	293	6,600
Selenium	9 [2]	0.10	0.05	90	180
Strontium	239	92	--	2.6	--
Vanadium	203	5.0	0.3	41	677
Zinc	36	50	0.2	0.7	180
Zirconium	37	15	--	2.5	--
Total	208,450				

[1] MATE is an abbreviation for Minimum Acute Toxicity Effluent.

[2] Concentrations obtained from spark source mass spectrometry were used when inductively coupled plasma optical emission spectroscopy provided upper limit data only.

SOURCE: Leavitt *et al*. (68)

TABLE 5-32. REPRESENTATIVE COMPOSITION OF CONVENTIONAL HIGH SULFUR RESIDUAL OIL DERIVED FROM VENEZUELAN CRUDE

Parameter	Value
Sulfur	2.2%
Carbon	86.25%
Hydrogen	11.03%
Nitrogen	0.41%
API gravity	17.3
Viscosity	3138. SSU @ 38°C (100°F)
Carbon	12.51%
Hexane insoluble	10.33%
Ash	0.08%
Trace Metals	
Vanadium	350 µg/g
Nickel	41 µg/g
Sodium	25 µg/g
Iron	13 µg/g

SOURCE: Goldstein and Siegmund (70)

TABLE 5-33. PARTIAL COMPOSITION OF PARTICLES EMITTED FROM OIL-FIRED FURNACE BURNING HIGH SULFUR RESIDUAL FUEL OIL DERIVED FROM VENEZUELAN CRUDE

	COMPOSITION			
Size Fraction (µm)	Carbon (% in particulate)	Inorganic Ash (% in particulate)	V_2O_5 (as % of Inorganic Ash)	Na_2O (as % of Inorganic Ash)
>10	79.4	10.1	41.6	1.7
1-10	70.7	18.1	63.7	1.8
< 1	30.1	57.1	58.2	3.4

SOURCE: Goldstein & Siegmund (70)

Kukin (72) discussed addition of metal-containing additives to make boilers cleaner, cut corrosion, and reduce stack emissions of hydrocarbons and sulfur trioxide. Significant fuel additives were reported to contain magnesium oxide (with or without small amounts of aluminum oxide or hydrate), manganese, and magnesium oxide with manganese. Presumably the use of additives containing manganese would increase manganese emissions to the atmosphere.

Suprenant et al. (73) have reported the results of a preliminary emissions assessment of the air, water and solid waste pollutants produced by conventional stationary combustion systems. This report summarizes system characteristics. It also summarizes pollutant emissions from unit operations for 56 source classifications. Trace element emissons are covered.

5.7 TRACE ELEMENT EMISSIONS FROM INCINERATION OF SOLID WASTE MATERIALS

Several reports have described emissions from systems that incinerate solid wastes. Wastes which have been incinerated include municipal refuse, sewage sludge and trash. Atmospheric emissions of particles have been described. In addition, characteristics of collected ash and of waste water streams have been reported. The reports identified in the literature search are described briefly below.

5.7.1 Trace Element Emissions from Municipal Incinerators

Greenberg et al. (74, 75) have reported concentrations of trace elements in particles emitted from three municipal incinerators. Two of the incinerators served largely residential areas around Washington, D.C. The other incinerator served a mixed industrial, commercial, residential area in Eash Chicago and Hammond, Indiana.

The Alexandria incinerator near Washington, D.C. had two furnace trains, each capable of incinerating 140 metric tons of refuse daily. Effluent gases were passed through a water spray baffle to remove some of the fly ash. The temperature of the gases leaving the stack was 260°C. Total particulate emissions from this incinerator were approximately 2.8 kg of suspended particles per metric ton of refuse burned.

The Solid Waste Reduction Center #1 (SWRC) (also near Washington, D.C.) contained six furnace trains. Each train was capable of incinerating 230 metric tons daily. Particles were controlled by mechanical separators and electrostatic precipitators. Total particulate emissions from this facility were 0.46 kg per metric ton of refuse burned.

The Nicosia Municipal Incinerator in East Chicago Indiana had two furnace trains. Each train was designed to incinerate 204 metric tons of refuse daily. Particulate emissions were controlled by a spray chamber followed by a three-stage, horizontal, plate-type scrubbing tower. The average total particulate emissions were about 4 kg per metric ton of refuse consumed.

The concentrations of 28 elements in the particulate emissions from the three facilities are listed in Table 5-34. The compositions of the suspended particles downstream from the particle control device were not the same as the compositions of the collected particles. Two extreme examples are cited below. The average concentration of lead in the collected particles from the Alexandria facility was 0.40 percent. The suspended particles from this facility were reported to contain 9.7 percent lead. The average chlorine concentration in collected particles from the SWRC #1 was 0.13 percent. The suspended particles from this facility averaged 14 percent chlorine.

Enrichment of several elements on small particles was observed. Elements which exhibited this enrichment pattern were:

antimony
arsenic
bromine
cadmium
cesium
chlorine
copper
indium
lead
silver
sodium
tin
tungsten
zinc

These elements were reported typically to have more than 75 percent of their masses in particles with diameters less than 2 μm.

TABLE 5-34 ORDER OF MAGNITUDE COMPOSITIONS OF PARTICLES EMITTED FROM THREE MUNICIPAL INCINERATION

	Element	Concentration (μg/g)					
		Alexandria		SWRC #1		Nicosia	
1.	Aluminum	16,000	± 8,000[1]	21,000	± 10,000	≃ 5,000.[2]	
2.	Antimory	2,400	± 2,400	2,400.	± 1,100	1,600.	± 800
3.	Arsenic	210.	± 100	310.	± 160	200.	± 90
4.	Barium	890.	± 570	990.	± 410	220.	± 130
5.	Bromine	2,600.	± 1,400	920.	± 520	880.	± 390
6.	Cadmium	1,100.	± 400	1,900	± 700	1,500.	± 400
7.	Calcium	23,000.	± 11,000	11,000.	± 3,000	--	
8.	Cesium	3.1	± 1.7	5.5	± 2.2	8.5	± 3.3
9.	Chlorine	200,000	± 50,000	140,000.	± 30,000	270,000	± 30,000
10.	Chromium	490.	± 350	870.	± 370	105.	± 17
11.	Cobalt	12.	± 7	5.4	± 2.5	2.3	± 0.5
12	Copper	2000.	± 1,200	1500.	± 500	1700.	± 300
13.	Gold	0.71	± 0.77	0.70	± 0.06	0.43	± 0.18
14.	Indium	6.5	± 5.4	3.6	± 0.7	6.5	± 0.7
15.	Iron	9000.	± 3,000	7100.	± 1,400	3300.	± 1,500
16.	Lanthanum	3.8	± 2.6	4.6	± 1.1	2.9	± 1.6
17.	Lead	97,000.	± 26,000	77,000.	± 11,000	69, 0.	± 10,000
18.	Magnesium	6,800	± 2,500	3,600	± 700	28,000	± 8,000
19.	Manganese	1,500	± 1,400	410	± 110	270	± 80
20.	Nickel	200	± 80	170	± 70	79	± 29
21.	Samarium	≃0.8[2]		0.62	± 0.15	0.40	± 0.20
22.	Selenium	23.	± 21	39	± 29	49	± 37
23.	Silver	390.	± 360	1000	± 800	110	± 80
24.	Sodium	98 000.	± 28,000	65,000	± 13,000	82,000	± 13,000
25.	Thorium	1.8	± 1.4	≃3[2]		0.37	± 0.28
26.	Tin	10,700.	± 1,500	10,800	± 1,100	12,900	± 1,600
27.	Titanium	2,900	± 1,400	3,600	± 2,000	≃500[2]	
28.	Tungsten	17	± 11	22	± 8	≃8[2]	
29.	Zinc	120,000	± 60,000	130,000	± 50,000	110,000	± 30,000

[1] Uncertanties are standard deviations

[2] Only approximate concentrations could be reported because blank values were high.

SOURCE: Greenberg *et al*. (74).

Elements reported to have predominantly large particle distribution were:

- aluminum,
- calcium,
- lanthanum,
- scandium, and
- titanium.

Some elements were observed to have mixed size distributions. These elements were:

- chromium
- cobalt,
- iron,
- manganese,
- selenium, and
- vanadaium.

The enrichment mechanisms were said to be complex.

The authors estimated the contributions of incinerators to trace elements in urban aerosols. They concluded that emissions from incinerators were major sources of airborne antimony, cadmium, and zinc. They also suggested that incinerators might be major sources of airborne indium, silver and tin in many areas.

The authors did not measure mercury emissions. They noted that others (76) had indicated that incinerators are large sources of vapor phase mercury emissions.

5.7.2 Metals in Municipal Solids Waste and Aqueous and Solid Effluents from Municipal Incinerators

A group at the Bureau of Mines in College Park, Maryland, has been investigating metals in municipal waste and effluents from municipal incinerators. Law *et al*. (77, 78, 79) and Haynes *et al*. (80) have reported trace element concentrations in the combustible fraction of municipal waste.

In addition to the reports cited above, Law (81) has reported concentrations of 26 dissolved metals in aqueous effluents from three municipal incinerators. The concentration trends as a function of time were studied in the recycled spray chamber waters and recycled quench waters of one incinerator. The spray chamber was designed to remove fly ash. The quench waters were applied to bottom ash.

None of the metal concentrations in the effluents exceed local sewer regulations. Concentrations of zinc in recycled spray chamber waters reached levels possibly detrimental to biological wastewater treatment. Concentrations of several metals in the effluents exceed drinking water standards. Several metals were observed to be enriched in the effluents relative to city water. The pH of the effluent streams was observed to decrease as the operating temperature of the incinerator increased.

Law (82) also reported concentrations of several elements in solids filtered from municipal incinerator effluents. Chlorine, copper, silver and titanium were reported to be present in concentrations comparable to those found in low grade ores.

Several elements in these filtered solids were found in concentrations to be one to three orders of magnitude above average crustal abundances. These elements were:

antimony
arsenic
cadmium
chromium
copper
lead
mercury
silver
tin
zinc.

Ash collected in particle collection devices was reported to be at least an order of magnitude higher than coal fly ash in the following elements:

antimony
cadmium
lead
nickel
silver
zinc.

The elemental concentrations of ash from particle collection devices and bottom ash were reported to be similar. Elemental concentrations in the ashes remained constant, within experimental error, over a period of time and for different geographical locations.

5.7.3 Trace Element Emissions from Municipal Incinerator Near Langley Station, Virginia

Singh (83) determined the elemental composition of aerosol particles from a municipal incinerator. The particles were aerodynamically separated into eight size fractions. The nominal aerodynamic diameters ranged from 0.43 μm to 20 μm. Elemental analysis was carried out using a charged particle inducted X-ray emission technique. Elemental concentrations were calculated as concentrations in the aerosol. Sensitivities were reported to be in the ng/m^3 range for most elements with atomic number 11 and above.

The size distribution of the collected particles was determined to be biomodal. One mode was centered at 0.54 μm and the other mode was centered at 5.6 μm. Potassium and sulfur were reported to show a strong tendency to concentrate on aerosol surfaces. Manganese and nickel were reported to show a weaker trend for surface preference. Other elements were reported to show no trend for surface preference.

5.7.4 Seleniun in Smoke from Open Trash Burning

Shendrikar and West (84) reported the analysis of smoke from open trash burning for selenium content. Selenium was reported to be in the oxide form and was trapped by impingement in distilled water. The methylene blue catalytic method was used to measure selenium concentrations in the impinger solutions. Selenium content of the smoke was related to the selenium content of the trash. Concentrations of selenium dioxide as high as 273 μg/m^3 were reported when dry wood chips were burned.

5.7.5 Other Reports of Emissions from Refuse Incineration

Rigo et al. (85) prepared a summary of engineering data and criteria from feasibility studies covering the preparation and use of refuse as fuel. They mention that if plated metals are fed into the sterilizer, high concentrations of antimony, cadmium, lead, tin and zinc can be emitted as a submicron aerosol. They recommended that efficient particle collection devices such as electrostatic precipitators, scrubbers, or baghouses be used on facilities burning refuse.

Shannon and Schrag (86) have reported uncontrolled particulate emissions of 0.94 to 9.4 grams per million joules for modern heat recovery incinerators. Emitted particles were reported to have significant concentrations of trace or heavy metals.

Niessen (87) reported a particulate emission factor of 12 kg per metric ton of refuse. This factor was based on the average of particulate emissions from 50 incinerators.

A feature article in Environmental Science and Technology in 1971 (88) stated that incineration and recycling of ferrous scrap was the major source of atmospheric emissions of cadmium in 1968.

H.F. Sidney (89) has reported that most potentially hazardous metals are not found in significant amounts in emissions from well controlled incinerators.

Hall (90) lists incineration of refuse as a source of lead in the atmosphere.

Devitt (91) stated that particulate emissions are the most apparent problem when wastes are used as fuels. He also stated that calcium, copper, iron, lead and zinc emissions were increased over coal when refuse fuel and coal were co-fired.

Gross *et al.* (92) reported metal emissions from the burning of a mixture of sewage and sludge. Cadmium had the lowest emission rate (3 g/hr) of the metals measured, while lead had the highest (680 g/hr). Emission rates for several other trace metals were between these extremes. When the ratio of refuse to sludge was changed, cadmium again had the lowest emission rate (3 g/hr) but zinc had the highest (966 g/hr).

Cho and Chambers (93) reviewed the use of solid waste as a supplementary fuel in power plants. They reported that in one test emissions of hydrogen chloride and mercury vapor were not significantly affected by the combined firing of refuse and coal. In another test, firing of 5-20 percent refuse with Orient 6 coal increased chloride emissions by about 30 percent.

J.W. Jackson (94) has reported the results of a bioenvironmental study of emissions from refuse derived fuel.

5.8 TRACE ELEMENT EMISSIONS FROM WOOD BURNING FACILITIES

Very little information was found in the literature describing emissions from wood burning facilities. Hall *et al*. (95) gave the composition of wood ash as reported by Brown (96). These values were listed in Table 5-35. Hall also reported that the emission factor (97) for particles from wood waste burning boilers was 90.3 kg per million joules (0.210 lbs per million). This factor was used to calculate elemental emissions based on heating value of the hogged fuel. The results of the calculations also are given in Table 5-34.

The information given in this table should be taken only as an order-of-magnitude estimate of emissions. The emission factor is an average value. No information is given as to what controls, if any, this level of emissions corresponds to. The assumption was made that the composition of the particles emitted would be the same as the ash. This assumption is not valid for coal-fired facilities and may well not be valid for wood fired facilities. In addition, the concentrations in this instance were determined by a spectrographic analysis usually considered to give only order-of-magnitude accuracy.

5.9 NEEDS FOR FURTHER STUDY CONCERNING TRACE ELEMENT EMISSIONS FROM SCCP

Many measurements have been made of trace element emissions from SCCP's. These measurements have usually been made at a specific site under a specific set of conditions. These data are useful for indicating ranges of trace element emissions. But no empirical or theoretical framework exists for predicting trace element emissions from a given facility with a high degree of confidence.

It is convenient to discuss needs for further study in the same order that was used for compilation of emission data earlier in this section. Atmospheric emissions from coal-fired facilities will be discussed first.

TABLE 5-35. COMPOSITION OF HOGGED FUEL (WOOD AND BARK) ASH AND CALCULATED ATMOSPHERIC EMISSIONS FROM HOGGED FUEL BOILERS

Element	Concentration (μg/g)	Calculated Atmospheric Emissions Based on Heating Value (g/10^{12} joules)
Aluminum	3.6	325,000.
Barium	0.010	900.
Boron	0.003	300.
Calcium	2.9	260,000.
Chromium	<0.001	<90.
Copper	<0.001	<90.
Lead	0.003	300.
Magnesium	0.8	70,000.
Manganese	0.016	1,400.
Mercury	nil	nil
Nickel	<0.001	<90.
Potassium	0.3	27,000.
Silicon	19.6	1,770,000.
Sodium	2.1	190,000.
Strontium	0.002	200.
Titanium	0.1	9,000.
Vanadium	<0.001	<90.
Zirconium	0.006	500.

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[1] Based on 90,300 grams of total particulate emissions per 10^{12} joules heating value in fuel.

SOURCE: Hall _et_ _al_. (95). Data orginially from Brown (96) and USEPA (97).

Next, emissions from coal-fired facilities to land and water will be considered. Finally, emissions from facilities burning fuels other than coal will be presented.

5.9.1 Needs for Further Study Concerning Trace Element Emissions to the Atmosphere from Coal-Fired Facilities

Much of the data concerning atmospheric emissions from coal-fired facilities have been compiled [Ray and Parker (98); Ragaini and Ondov (99)] and recompiled [Torrey (100)]. Too few efforts have been made to analyze and interpret the data.

As a part of the current program, atmospheric emission data from several studies were collected and normalized to the heating value of coal. The values calculated were presented in Tables 5-1 and 5-2. A cursory examination of these data reveals that atmospheric emissions of trace elements vary over a wide range. These data indicate that poor particulate control permits release of many trace elements to the atmosphere. Conversely, good overall particulate control will reduce atmospheric emissions of most trace elements from these facilities, but the degree of control for each element is not easy to define.

To develop a predictive capability for atmospheric emissions from these sources a two-step approach will be required. First, currently available data need to be analyzed and interpreted. This analysis and interpretation of programs should be planned to fill the gaps.

Subjects that should be examined when available atmospheric emission data are scrutinized are listed below.

- Concentrations of trace elements in coal and expected range of concentrations for coal from a given source need to be established as a function of time (i.e., as different parts of the seam are mined or delivered).
- Effects of the concentrations of major inorganic species in coal ash upon trace element composition of ash need to be identified.
- Effects of association of trace elements in the coal (i.e., inorganic vs organic and chalcophile vs lithophile associations) upon trace element partitioning in the ashes need to be studied.

- Reliability of sampling techniques and methods of chemical analysis need to be determined.
- Effects of boiler configuration on trace element partitioning need to be studied.
- The effects of temperature profiles in boiler and particle collection devices upon trace element partitioning in the ash need to be determined.
- Effects of overall efficiency of particle collection devices on trace element emissions to the atmosphere need to be measured.
- Effect of particle collection efficiency *vs* particle size curve on emission of certain trace elements needs to be established.
- Elements which may escape in the vapor phase need to be identified.
- Factors which lead to enrichment of certain elements in very small particles and/or on the surface of fly ash particles need to be evaluated.

5.9.2 Needs for Further Study Concerning Trace Element Discharge to Land and Water from Coal-Fired Facilities

Data regarding transfer of trace elements to land and water have been examined more thoroughly than data for atmospheric emissions. Hart *et al*. (34) and Coltharp *et al*. (38) have prepared compilations of existing data and have identified data gaps and research needs. The major needs identified by these studies relating to trace element emissions are summarized below.

- A broader data base on the origin, chemistry and ultimate pathways of trace elements in waste streams needs to be developed.
- Ash characteristics relating to field disposal characteristics (especially leachability) need to be correlated with boiler type and coal characteristics.
- Characteristics of scrubber sludge (relating to fixation reactions, leachability, and physical properties) need to be correlated with scrubber type and operation.
- Studies are needed that can be used to develop correlations between laboratory leaching data and field leaching data.
- To determine the effects of leachate on groundwater, studies need to be made to correlate laboratory permeability measurements and laboratory measurements of leachate composition with field data on these parameters. Studies of interaction of leachate with soils are needed.

- Liner permeabilities need to be studied under field conditions.
- The variability of trace element contents of ashes and sludges needs to be established as a function of time.
- Leachability of ashes and sludges under different disposal schemes needs to be studied.
- Disposal sites currently in operation need to be characterized with respect to trace element emissions.
- Analytical methods and sampling techniques need to be evaluated.
- Effects of process changes on ash and sludge characteristics need to be studied.
- The potential for recovery of valuable materials present in trace amounts in ashes needs to be reevaluated.
- Disposal procedures that would allow future recovery of valuable trace elements should be developed.

5.9.3 Needs for Further Study Concerning Trace Element Emissions from Combustion of Oil, Municipal Refuse, and Wood

Information on trace element emissions from oil-fired combustion processes is scant. The chemical composition of particulate emissions as a function of trace element concentrations in oil needs to be more firmly established.

The apparent uniformity of atmospheric emissions from municipal refuse incinerators needs to be confirmed. The leachability of municipal refuse ash needs to be studied further.

Characteristics of wood ash need to be more firmly established.

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SECTION 6

ENVIRONMENTAL AND HEALTH EFFECTS

Trace metal emissions from stationary conventional combustion processes (SCCP's) are cause for growing interest and concern because of their environmental and health effects. The current shift in principal feedstocks for electrical utility generation from natural gas and fuel oil to coal has stimulated the current interest in trace metal emissions. Many of the trace metals present in the effluent streams from a typical coal-fired plant are toxic. Another important factor in assessing the potential for adverse impacts from these emissions is the low ambient level of these elements in the atmosphere and natural waters (see Section 2). To date most of the regulatory emphasis concerning coal utilization has centered on SO_x, NO_x, and fly ash in general. Effective control measures are well known for these criteria pollutant classes, but recently the limitations of these systems for control of trace metal emissions, particularly atmospheric emissions, have been noted.

Trace metals are present in fuel oils as well as all coal types, but their relative concentrations in coal are of the greatest concern. Many of the trace elements in coal are required micronutrients for vegetation which accounts for their presence. The concentrations of trace metals in coals varies over a wide range, but almost all of the naturally occuring trace elements are present in coal. These trace elements are released to the environment during coal preparation as well as combustion in potentially toxic amounts (1). Combustion of coal results in a general enrichment of trace metals in the residual ash. Of the ten trace elements most enriched in coal ash, nine are potentially hazardous to humans or animals: antimony, arsenic, beryllium, cadmium, lead, molybdenum, selenium, sulfur, and uranium (2).

It is the emission of these and other toxic trace metals, particularly in the atmosphere, that is of greatest concern. Numerous studies have concluded that a high degree of correlation exists between community air pollution and mortality or morbidity attributable to pulmonary disease (3). Total trace metal emissions from coal-fired electrical generation facilities constitute a sizeable percentage of total trace metal contributions from anthropogenic sources. Projected increases in total emissions due to increased coal use in the future may result in significant elevations in trace metal concentrations in the atmosphere. These increases will undoubtedly be paralleled by increased incidence of chronic diseases related to long-term trace metal exposure (4). Several recent studies have compared the occupational and public health effects of generating electricity from coal, uranium and oil. Dosage calculations based on airborne emissions concluded that uranium offers less of a health hazard as a fuel than coal (5,6) (See Section 7). These analyses are based on emission rates from plants with conventional control units in place. Advances in control technology for trace metal emissions can be expected to reduce the occupational and public-health risks from coal use.

6.1 ELEMENTS OF SPECIFIC CONCERN

Several elements have received individual attention in the literature with regard to the environmental and health aspects of their emission from coal-fired plants. Another class of elements deserve special attention because of their known carcinogenic, teratogenic, and oncogenic effects.

Fluorine

Even though fluorine is not a trace metal, its emission from coal-fired plants is of special concern. Other major sources of fluorine pollution are the production of phosphate chemicals and fertilizers and several metallurgical manufacturing processes. The majority of the problems related to fluoride emission to the atmosphere involve deleterious effects on vegetation and animals that have ingested contaminated vegetation (7). Direct inhalation of fluorine gas or fluorine-contaminated fly ash particles by animals is less significant than uptake through contaminated forage and soil (8).

A summary of information concerning ecological and health effects of fluorine is presented in Section 6.6.

Mercury

The most important anthropogenic sources of environmental mercury in the U.S. are chloralkali plants, seed-dressing agents, smelting operations, and fossil fuel combustion. Natural sources are geothermal processes and the land mass itself (9). At 1970 rates of coal consumption, between 275 and 1800 tons of mercury were being released to the atmosphere annually in the U.S. This estimate is based on its average concentration in coal, between 0.5 and 3.3 ppm. Mercury is emitted primarily as a gas from coal combustion. It is a highly toxic element which is concentrated in many food chain processes, particularly in the aquatic environment. Inorganic mercury is converted by microorganisms to methyl mercury which is much more readily adsorbed, and more slowly excreted than elemental mercury.

Numerous studies (10, 11, 12) have reported a relationship between increased mercury contamination and an increase in the occurrence of mercury poisoning in wildlife and human populations. It is a known carcinogen, teratogen and oncogen which can induce harmful effects at very low levels. Because it is emitted primarily as a gas, current control methods designed to reduce particulate emissions are not effective. This fact and the known toxic and bioaccumulation effects have earmarked mercury as a trace metal of particular concern.

Selenium

Selenium is a semimetallic element with known environmental and health effects. A few studies have focused on the potential hazards associated with its increasing concentration in the ambient environments. Andren et al. (13) calculated that 1.5 to 2.5 times as much selenium is mobilized through coal burning as by natural weathering. The majority of the selenium released from a coal-fired plant to the atmosphere exists in the vapor phase or attached to particles which are not removed by electrostatic precipitators; however, the bulk of the selenium entering a plant leaves as part of the solid waste. Stahl (14) reviewed the literature concerning selenium and its compounds as air pollutants. Atmospheric selenium is known to cause irritation of the eyes, nose, throat and respiratory tract of humans, and, under conditions of prolonged exposure, gastrointestinal disorders. It is also a known carcinogen and increased atmospheric concentrations will increase the total body burden of this toxic element.

Carcinogenic, Oncogenic, and Teratogenic Elements

Carcinogenic agents may be defined as those that are capable of producing cancer in a tissue upon exposure. Many of the trace metals emitted from coal-fired plants -- arsenic, beryllium, cadmium, chromium, cobalt, mercury, and nickel are known carcinogens. All of these elements and lead are oncogenic (tumor-producing) as well. Except for arsenic, dosage-response data for the carcinogens listed above can be found in the health effects summaries presented in Section 6.6. Teratogenic may be defined as inducing structural and/or functional deviation in an embryo during its development, resulting in congenital birth defects. Barium, cadmium, lead, lithium, mercury, and selenium are all considered teratogenic. Dosage-response information for each of these known teratogenic elements can be found in the health effects category in Section 6.6.

Carcinogens, as a class of pollutants, must be considered somewhat differently than other toxic elements. Most other toxic elements have a threshold limit value (TLV) which is associated with the minimum exposure (as body burden) level of the pollutant at which health effects attributed to that specific pollutant may be expected to occur. Exposure or intake of specific pollutants in amounts below the TLV may cause health effects due to unknown synergisms with other pollutants present, but the health effects that occur cannot, at our present level of understanding, be related directly to one specific pollutant.

Carcinogens, on the other hand, do not have a TLV associated with their potential for health effects. Current theory on carcinogenic responses holds that any increase in the exposure or intake levels of a particular carcinogen may be expected to increase the occurrence of cancer in an affected population of sufficient size. The dosage response information presented for carcinogens in Section 6.6 suggests minimum acute response levels of these carcinogens (i.e., occurrence of cancer in a relatively high percentage of organisms under laboratory test conditions), but this does not imply that carcinogen levels below this amount will not result in some increased incidence of cancer.

Chronic exposure to low level carcinogen concentrations and the potential for synergisms at low levels between these carcinogens is a point of concern for many public health officials. At least a few of the trace elements that are known carcinogens may be emitted at relatively high concentrations from coal-fired plants equipped with present day control technologies. Under worst-case conditions, the ambient concentration of these elements may be significantly elevated by SCCP's.

6.2 ENVIRONMENTAL TRANSPORT MECHANISMS

The principal environmental transport mechanisms are summarized in Table 6-1. Material transfer of trace metals between ecological compartments is difficult to impossible to quantify. The exact nature of the transfer process will be dependent on a multitude of factors. The specific chemical form of a pollutant, cycling processes, biological uptake and transfer rates, bioaccumulation effects, and type of parent soil or sediment material where trace elements are deposited will be the principal determinant of pollutant transfer in the environment once these chemical agents are released from a plant. All of these factors are site specific, making generalizations about the overall process difficult. Nevertheless, a few generalizations can be made before examining specific results in the literature.

Source to Sink Routes

Mass balance studies on coal-fired plants equipped with an ESP or equivalent efficiency particle control units indicate that approximately one percent of the total ash fraction of the plant is emitted from the stack. Typically the remaining 99 percent forms the bottom ash and precipitation ash fractions. These fractions are often combined and trucked or slurried to an ash pond disposal site. An estimate of annual coal consumption

TABLE 6-1. MAJOR TRACE METAL PATHWAYS AND TRANSPORT MECHANISMS

Atmosphere To:

1. Man - inhalation
2. Animals - inhalation
3. Plants - direct absorption
4. Soil - deposition
5. Surface water - deposition

Soil To:

1. Man - inhalation of dust; ingestion
2. Animals - inhalation of dust; ingestion
3. Plants - root uptake
4. Surface water - deposition of dust; erosion by surface runoff
5. Groundwater - leaching from surface soils

Surface Water To:

1. Man - ingestion
2. Animals - ingestion; absorption
3. Plants - root uptake; absorption
4. Soil - infiltration
5. Groundwater - infiltration

Groundwater To:

1. Man - ingestion
2. Animals - ingestion (stock watering)
3. Plants - root uptake, absorption (irrigation)
4. Surface water - spring and seep discharge
5. Soil - upward and lateral migration

Plants To:

1. Man - ingestion
2. Animals - ingestion
3. Soil - decay and demineralization
4. Surface water - decay and demineralization

Animals To:

1. Man - ingestion
2. Soil - excretion; decay; demineralization
3. Surface water - excretion; decay; demineralization

Man To:

1. Soil - excretion
2. Surface water - excretion

for a 500 MW boiler is 1.88 x 10^6 tons/years ±10% (15). Assuming a typical ash fraction of 15 percent of the total coal mass, then approximately 2.80 x 10^6 tons/year ±10% of materials will end up as precipitator ash or bottom ash, and 2.82 x 10^6 tons/year ±10% will be emitted as gaseous or particulate effluent.

Trace element partitioning is different from the total mass partitioning discussed above with a larger fraction of the total trace element content of the coal being emitted from the stack (see Section 5). The remaining trace element fractions are contained in the bottom ash and precipitator ash. The major source of trace metal pollutants that effect terrestrial and aquatic organisms is stack emissions; however, the potential does exist for pollutant transfers from ash or scrubber sludge pond leachates entering either the ground water or surface-water systems. Cooling pond water, which is associated with many typical coal-fired plant systems, is another potential source of contamination to surface and ground water. It is also the primary aquatic environment where significant pollutant contamination and possible ecological effects can be expected to occur.

Solid Waste Emissions

The solid waste fraction contains the bulk of the trace metals from coal use. This waste stream is generally transported by mechanical means to a disposal pond site. Transport of trace metals from the disposal pond via leaching to other ecological compartments in the environment is determined by several factors:

- the type and thickness of any clay or plastic liner that might be used,
- the permeability, cation exchange capacity, or porosity, of the substrate; in general the mobilization-attenuation characteristics of the soil for the specific elements under consideration,
- soil and pond liquor pH,
- substrate trace element concentration, and
- the proximity of the disposal pond site to the ground water table and/or surface water.

The degree of movement of trace element pollutants from an ash pond disposal site will be a function of the site-specific factors listed above. Generally, the solid waste disposal site will be an effective sink for most of the total trace metal mass entering the plant. Movement away from this sink will be relatively small in most cases.

Atmospheric Emissions

The gaseous and particulate waste stream emitted from a coal-fired plant to the atmosphere has the greatest potential for significant ecological and health effects as it moves through the environment away from the emissions source. When the effluent leaves the stack, the buoyant plume travels downwind spreading vertically and horizontally decreasing in trace element concentration by dilution with increasing distance from the plant. As the plume encounters the ground, some particles are deposited directly on the surface while others are reflected or "bounced" back into the atmosphere. The rate of deposition and the surface concentration are the principal factors that determine the degree and nature of impact that the atmospheric trace metal concentrations will have on a particular ecological compartment. Transport and deposition models are used to estimate surface concentration and deposition velocities. Site-specific factors necessary for these models include emission rate, wind data, precipitation data, meteorological stability class, type of terrain, temperature, and stack height.

It is these atmospheric trace metal emissions that constitute the greatest potential threat to man and his environment. Purves (16) has reported that concentrations of certain trace metals in Antarctica and Greenland are increasing due to global transport processes. General atmospheric circulation patterns from the industrialized temperate regions to the equator and then to the poles via the upper atmosphere can distribute regional pollutants globally. Since fine particles can behave analogously to a gas, the residence time in the atmosphere and potential zone of impact from even a single point source can be quite large. These effects are felt as added increments to ecosystems, which may vary considerably in background pollutant levels, whether natural or otherwise.

The above considerations reflect the difficulty in estimating probable sinks, as well as quantifying transfers between ecological compartments for atmospheric trace element emissions. Studies to date have shown only slight correlation at best of source emissions with measurable changes in atmospheric, soil, and biotic trace metal concentration even when examining effects of emissions relatively close to the source. Clearly, estimates of the specific effects of trace element emissions become very difficult, if not impossible at large distances. In any case, some general assumptions concerning the pathways of these pollutants through ecological compartments is possible.

- Surface deposition of trace elements on soils will be the major primary sink for most trace elements being emitted.
- The affected zone within the soil will be small, probably less than 5 cm deep in most cases.
- Some trace elements may be inhaled or absorbed directly by plants, animals, or man but most trace elements will enter the food chain after uptake by plants or ingestion of contaminated water or soil.
- Trace elements entering into a food chain may be concentrated and eventually removed from a given area by mobile organisms higher in the food chain, but most trace elements will be cycled rather than transported after deposition.
- Trace elements deposited on surface waters will probably be of less significance than those transported by erosional factors, whether they originate from natural or anthropogenic sources.
- The ultimate sinks for emitted trace elements will be determined by factors such as terrain, meteorological conditions, substrate characteristics, and proximity to surface water.
- Trace elements entering an aquatic environment will probably be cycled by organisms to a certain extent, eventually accumulating in bottom sediments.

- Removal of trace elements entering aquatic systems will be primarily by predation from animals or resource utilization such as fishing by man.

- The principal pathways of trace elements to man will be inhalation and ingestion of contaminated organisms.

6.2.1 Aquatic Pathways

Principal sources of trace metals from coal-fired plants include aerial deposition of stack effluent, coal pile runoff and plant washdown into cooling ponds, ash disposal pond leachate and overflow to surface and ground water systems and discharges from cooling ponds to surface water. Wood et al. (17) studied the environmental effects of coal ash landfill on trace metal concentrations in surface water, groundwater and aquatic biota near the site. Results showed elevated concentrations of As, Cr, Fe, Mn, and K. The movement of coal ash leachate through relatively impervious clay silt, and shale was fairly restricted. This factor, together with a minimal ground water flow in the area resulted in minimal contamination of adjacent surface and subsurface waters.

Guthrie and Cherry (18) studied the aquatic ecosystem associated with a coal ash basin drainage system to determine abiotic and biotic characteristics and mechanisms of trace metal removal. Results of this study indicate that sedimentation of suspended solids containing trace metals from the ash basin was the major removal mechanism. Less than 1% of the total mass of trace elements accounted for in their sampling was present in the water column. Approximately 85% of the trace elements were in the benthos samples (sediment and benthic organisms). Br, Ca, Cl, Cd, Na, Sb, Se, and Zn were more concentrated in the biotic forms than they were in the benthos samples.

Dressen et al. (19) compared trace elements extracted from electrostatic precipitator ash using nitric acid, hydrochloric acid, citric acid, distilled water, and ammonium hydroxide as extractants. Effluent waters at this plant were sampled to assess the elevation of trace element concentrations compared with intake waters. The results indicated a positive correlation between those elements most extractable by water (B, Fe, Mo, and Se) or acid (As, B, Cd, F, Mo, Nd, Se) and those elements most elevated in effluent waters (As, B, F, Mo, and Se). It was concluded that water in contact with the ash in the disposal pond was most contaminated by the five elements listed.

Alberts et al. (20) studied the relative availability of certain trace metals from fly ash under simulated leaching conditions and compare these results with trace element releases from Lake Michigan sediment. Lake Michigan surface waters have a relatively high concentration of fly ash particles which have an estimated residence time in the water column of one year before sedimentation. Chemical conditions present in the sediment apparently promoted release of Mn, Pb, and Zn, but not Fe, compared to the fly ash leaching results.

Roffman et al. (21) report slight elevations in trace element concentration in aquatic organisms present in a lake which is affected by the Four Corners plant, but no consistant trends were noted. Concentrations of trace elements present in aquatic plants, net plankton, and fish varied greatly. They also reported that the quality of seepage water from the ash pond and cooling lake was determined more by the mineral composition of the parent soil material than the presence of trace metals in the water or ash pond effluent which originated from plant operations.

A major interdisciplinary study conducted out of the University of Wisconsin at Madison (22) on the ecological effects of coal-fired steam-electric generating stations investigated the effects of trace element emissions on the aquatic system associated with the plant. Results to date indicate that aluminum and barium floc released from the ash basin may be contaminating benthic communities downstream.

Anderson and Smith (23) investigated the dynamics of mercury at a coal-fired plant -- cooling lake complex and found some elevation of mercury in lake sediments, but mercury concentrations in fish were unusually low. Thus, slight increases of certain trace elements such as arsenic and fluorine (19), calcium, magnesium, and sodium (21), and copper and chlorine (22) have been shown. These changes in trace element concentrations may be due to evaporative losses in the cooling lake which can concentrate dissolved constituents by a factor of 2.5 (19), or the addition of chemical agents such as chlorine used to prevent biofouling in condenser tubes (22, 21).

A very detailed modeling study by Wagenet et al. (24) attempted to simulate heavy metal transport to a lake from a hypothetical coal-fired plant in a semi-arid climactic region. Transport of Zn, Pb, Cr, Cd, and Hg to the lake over a 25 year period was modeled interfacing submodels describing atmospheric diffusion, soil erosion, precipitation, and soil chemistry. The results indicate that after 25 years, Hg-loading to the lake is predominately due to aerosol fallout on surrounding soils while a significant fraction, but less than the majority, of the Cd-loading to the lake is due to plant emissions. Pb, Cr, and Zn loading rates were primarily determined by their idigenous levels in the soil and not significantly affected by plant emissions. The major transport mode to the lake was soil erosion rather than atmospheric fallout. The results of this study are site-specific and would be different with different soil types and climactic conditions. Other studies have suggested that trace metal concentration increases due to atmospheric fallout from SCCP emissions are extremely small (21, 25).

6.2.2 Atmospheric Pathways

Atmospheric trace metal emissions have generally been considered the most important effluent when evaluating the environmental and health effects of coal-fired plants. This is mainly because the affected area is quite large; however, the extremely small concentrations of these trace elements after dilution in the atmosphere has inhibited field monitoring of their transport and deposition. Modeling is now often relied upon instead of empirical results. Only a few studies have documented elevations in trace metal concentration due to a particular plant's operation. Klein and Russel (26) investigated the degree of heavy metal deposition around a coal-fired plant and correlated the measured concentrations with wind patterns. Soil enrichment patterns for Cd, Co, Cr, Cu, Fe, Ni, Tri, and Zn corresponded to prevailing wind direction. The concentration of Hg, emitted predominantly in a gaseous state, was only slightly enriched in the soil downwind from the plant.

Raridon (25) compared measured and estimated air concentrations of Cr, Cu, Mn, Mi, and Pb. The values were close for Cr, Cu, Mn, but not Pb. Measured values for Pb were high, probably due to heavy traffic on a nearby road. Cadmium concentration in a nearby watershed was also correlated with predicted values obtained from a hydrologic model. The model used estimated air concentration and deposition as inputs. Roffman et al. (21) studied the potential impacts of the Four Corners Generation Power Plant. They were unable to account for any measureable effect that stack trace element emissions had on air concentrations around the plant. Numerous ecological studies have shown that trace metal deposition has resulted in measureable change in the concentration of some trace metals in plants and animals downwind from a plant. The results of these studies are presented in Section 6.3.

6.2.3 Terrestrial Pathways

After deposition, trace metal transport is a function of numerous factors. Trace element availability in a given soil is dependent upon the solubility of the elements in that soil solution, which in turn is controlled in part by the cation exchange capacity of the soil. The cation exchange capacity is determined by soil texture, organic matter content, the amount and kind of clay present, and the amount of surface area of the soil colloids (27). Heavier soils generally have higher exchange capacities than light sandy soils low in organic matter. Cations are usually less available in heavy soils. Certain trace elements such as beryllium (28) and copper (29, 30) are held more strongly than most cations by the cation exchange complex, and therefore are less mobile in the soil solution. Cations are generally bound more tightly in neutral or slightly alkaline soils. In acid soils they become more mobile due to increased solubility and their replacement on the cation exchange sites by hydrogen (27). In acid soil the more mobile, lower-valance forms of trace elements predominate over the less mobile, high-valence forms. Therefore, soils with a pH exceeding 6.5 may pose less potential cation toxicity problems (31).

In general, much of the trace element deposition, particularly the cationic forms, is retained in the surface layers of the soil and is not readily leached to lower horizons, except in very acid or sandy soils. Trace anions are usually more leachable than cations (32). Retention of trace elements in the surface soil layers protects ground water from contamination. Nevertheless, surface runoff, erosion, and wind blown dust may still contaminate aquatic systems (32).

Wagenet et al. (24) used a soil chemistry model that indicated aerosol deposited and indigenous heavy metals will persist in the soil surface layer with little downward movement. Soil erosion was estimated to be the major transport process for deposited trace metals. After a 25 year period, model results predicted that approximately 15% of the total heavy metals fallout is transported to a lake. The lake is considered the final environmental sink according to this study.

Elevated concentrations of trace metals in soils, plants, and animals due to coal-fired power plant emissions have been documented in several studies. Anderson and Smith (23) reported elevated Hg concentrations in soils downwind from a power plant in central Illinois. Raridon (25) and Klein and Russel (26) also reported elevated soil and plant trace metal concentrations due to coal-fired plant emissions.

6.3 ECOLOGICAL EFFECTS

6.3.1 Known Response of Aquatic Ecosystems

Many cases documenting responses of aquatic ecosystems to trace metal emissions are present in the literature. A summary of certain specific references in this regard follows. Section 6.6 provides a quick summary of the known ecological and health effects. It should be consulted when questions concerning a specific element arise.

Guthrie and Cherry (18) investigated trace metal effects on components of an aquatic ecosystem present in a coal ash basin drainage system. Br, Ca, Cl, Cd, Na, Sb, Se, and Zn were more concentrated in water column biota than in the benthic samples. Since the bottom sediments were determined to contain the majority by mass of the trace elements in question, the selective concentration and cycling of the elements listed above was suggested. The light metals were concentrated more in animals than plants (Figure 6-1).

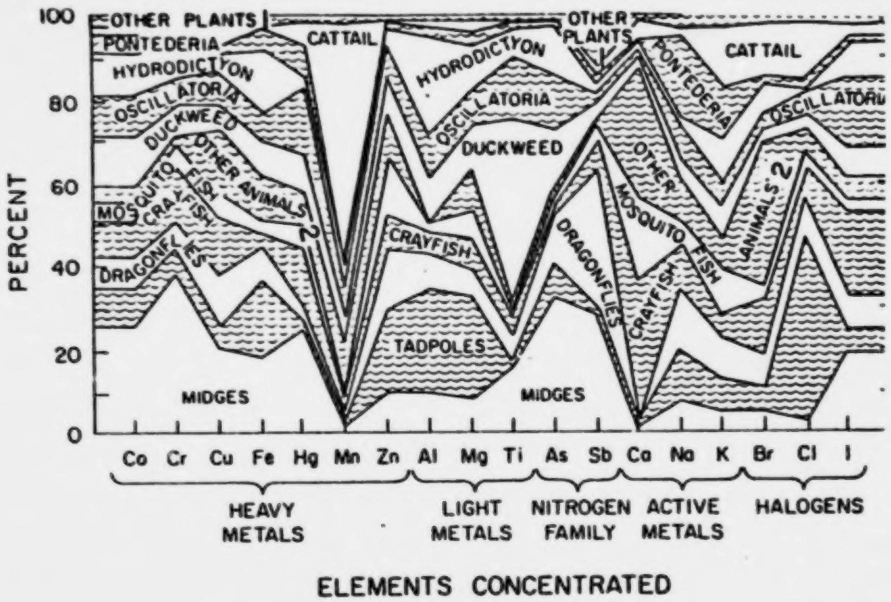

Figure 6-1. Relative accumulation of the most plentiful elements in the most abundant representatives of the food chain in all sampling sites. (1, includes bacteria and cypress; 2, includes clam and shrimp.)

SOURCE: (18)

Mosquito fish and crayfish were the dominant organisms with regard to Ca, Na, and K concentration. The benthic dwelling midges concentrated the largest number of trace elements (Co, Br, Cu, Fe, Sb, Hg, As) followed by tadpoles (Zn, Al, Mn, Cl). The active metals (Figure 6-1) Ca, Na, K, and halogens Br, Cl, and Cl were most concentrated by organisms in the drainage system. These elements, particularly the active metals group, will be rapidly and actively cycled in the food web of this system. In general, the concentration ability was generally lower in the plants and bacteria than animals as might be expected. Aquatic community diversity and stability increased with increasing distance from the ash basin suggesting a depressing effect on these ecosystem parameters perhaps due to trace element contamination.

Results of a five-day toxicity test indicated that organisms within the drainage system were able to survive at any point within the system. Organisms not indigenous to this system showed a variable resistance to the drainage system environment. Non-indigenous channel catfish and largemouth bass were most resistant to the toxicity tests. Non-indigenous shrimp, darters and salamanders were least resistant with shrimp being the most sensitive. These results indicate that, for this case at least, either indigenous populations are selectively resistant to the trace element environment, or indigenous species acquire some form of resistance after birth.

Other studies have indicated a depression in some component of aquatic ecosystems which are directly affected by trace element contaminants from coal-fired plant effluents (22). Spigarelli *et al*. (33) are studying the effects and interactions of fossil fuel pollutants on Lake Michigan zooplankton. Planktonic crustaceans, according to the authors, appear to be more sensitive to certain pollutants than either phytoplankton or fish, and thus may be critical in determining aquatic ecosystem responses. The long-term effects of elevated Cd concentrations in Lake Michigan were investigated using laboratory populations of *Daphnia galeata mendotae*. Results indicate significantly increased prenatal mortality at all levels down to 1 ppb Cd and significant effects on average population numbers and biomass down to 4 ppb.

Helmke (34) has shown that concentrations of Cr, Ba, and Sb are increasing in aquatic insects taken from a fly-ash pond drainage system since a relatively new power plant started operations. Samples from pre-operational years and from sites not affected by the ash pond were examined to demonstrate present trends. Roffman *et al*. (21) found considerable variation in trace element concentrations of aquatic organisms present in a coal-fired plant cooling lake. Trace element concentrations in aquatic plants, net plankton and fish samples varied greatly, but some food web concentration effects were noted.

6.3.2 Known Responses of Terrestrial Ecosystems

The body of literature reviewed for this subsection can be divided into those investigations that could account for changes in trace element concentration of terrestrial biotic components, and those that could not. Factors that could account for these differing results include study and detection methods, age of plant operations, specific elements under investigation, representative species sampled, and control technologies involved in emission systems. As such, the following results which may seem contradictory at times should not be surprising. Since no method of evaluating impacts has been standardized, variable results from independent investigations can be expected at this point. This demonstrates the need for more basic data to begin to resolve apparent discrepancies. Before reviewing the literature concerning specific impacts on terrestrial ecosystems, a short treatment of trace metal effects on vegetation is presented.

Trace element emissions may directly affect the aerial portions of plants in a number of ways. The vapor form of some elements, such as mercury, can be absorbed by the aerial plant parts (35, 36, 37, 38). Particles deposited and retained on leaf surfaces can clog stomata, decrease photosynthesis, or interfere with other leaf functions (39). Toxic concentrations of trace metals such as lead and arsenic, which are normally translated from the roots to the tops of plants, may be ingested by livestock or other herbivores feeding on surface contaminated plants (40). Particles originally deposited on plant surfaces may reach the soil through leaf litter or be incorporated into the soil by washing of plant surfaces by rainfall (41).

Plants possess the ability to concentrate essential mineral elements from rather dilute soil solutions. When soil concentrations of essential microelements such as zinc, manganese, cobalt, copper, and molybdenum are increased, plants may continue to accumulate these elements to toxic levels. Unessential elements such as cadmium or nickel may also be accumulated in the plant parts. Factors such as age, plant growth stage, or water stress and plant rooting characteristics may affect uptake of trace elements. Little and Martin (41) found most of the acetic-acid soluble lead, cadmium, and zinc in the upper 3 cm of heavily polluted soils near a large lead/zinc smelting complex. In these soils, plants with shallow spreading roots are probably exposed to more toxic concentrations than deeper rooting species. Furr et al. (42) grew various vegetables, grain and forage crops in fly ash-amended soil. Their results indicated that concentrations of As, B, Mg, and Se were greater in crops grown on fly ash-amended soil than control crops grown on soil not amended with fly ash. Table 6-2 presents the probably available form, average composition range, and suggested tolerance levels of certain heavy metals for selected agronomic crops.

Strojan and Turner (43) investigated the effects of trace element emissions on soils and plants near the Mohave Generating Station. Concentrations of Cu, Ni, Pb, S, and Zn were significantly higher in surface soils than in subsurface soils (10-20 cm). Sulfur concentrations in Ambrosia dumosa leaves and Cu concentrations in Larrea tridentata leaves decreased with increasing distance from the plant. Helmke (34) found that from 5 to 32 percent of the total amount of aerosolic dust on oak leaves near a coal-fired plant was fly ash. Isolated samples of leaves showed damage associated with particles of fly ash.

Horton et al. (44) measured trace element concentrations in soils and vegetation near a plant which had been in operation over 20 years. Significant effects of stack releases upon concentrations of Ba, Be, Cu, Hg, Mn, Sr, and Se in soil, Be, Co, Mo, Sr, and V in vegetation, and Co and Mn in groundwater were noted.

Mosses and lichens have been proposed as good indicators of trace metal pollution by a number of sources (46) because they tend to derive most of their inorganic constituents from the atmosphere. A study conducted around the Allen Steam Plant did not show excessive Hg or other heavy metal concentrations in mosses collected near that plant. The conclusion of this report was that the Allen Steam Plant had no detectable effects on trace

TABLE 6-2. PROBABLE AVAILABLE FORM, THE AVERAGE COMPOSITION RANGE FOR SELECTED AGRONOMIC CROPS, AND SUGGESTED TOLERANCE LEVELS OF HEAVY METALS IN AGRONOMIC CROPS WHEN USED FOR MONITORING PURPOSES*

	Probable Available Form	Common Average Composition Range* ppm	Suggested Tolerance Level ppm
		Cations	
Barium	Ba^{++}	10-100	200
Cadmium	Cd^{++}	0.5-0.20	3
Cobalt	Co^{++}	0.01-0.30	5
Copper	Cu^{++}	3-40	150
Iron	Fe^{++}	20-300	750
Manganese	Mn^{++}	15-150	300
Mercury	Hg^{++}	0.001-0.01	0.04
Lithium	Li^{+}	0.2-1.0	5
Nickel	Ni^{++}	0.1-1.0	3
Lead	Pb^{++}	0.1-5.0	10
Strontium	Sr^{++}	10-30	50
Zinc	Zn^{++}	15-150	300
		Anions	
Arsenic	AsO_4^{-}	0.01-1.0	2
Boron	HBO_3^{-}	7-75	150
Chromium	$CrO_4^{=}$	0.1-0.5	2
Fluorine	F^{-}	1-5	10
Iodine	I^{-}	0.1-0.5	1
Molybdenum	$MoO_4^{=}$	0.2-1.0	3
Selenium	$SeO_4^{=}$	0.05-2.0	3
Vanadium	VO_3^{-}	0.1-1.0	2

* Average values for corn, soybeans, alfalfa, red clover, wheat, oats, barley, and grasses grown under normal soil conditions. Greenhouse, both soil and solution, values are omitted.

Values are for corn leaves at or opposite and below ear leaf at tassel stage; soybeans, the youngest mature leaves and petioles on the plant after first pod formation; legumes, upper stem cuttings in early flower stage; cereals, the whole plants at boot stage; and grasses, whole plants at early hay cutting stage.

SOURCE: (45)

element concentrations in the vicinity. In a separate study investigating trace element measurements around the Allen Steam Plant, Auerbach (47) has found no appreciable part of soil trace element concentration which could be attributed to the steam plant.

Roffman et al. (21) investigated trace element concentrations near the Four Corners Plant. They examined soils, vegetation, and domestic and wild animals for elevated trace element concentrations due to power plant emissions. No significant effects were found.

6.3.3 Bioaccumulation Effects

Bioaccumulation by organisms may be defined as the accumulation of higher concentrations of chemical substances than naturally occur in their environment. Plants may selectively concentrate certain trace elements necessary for normal metabolism via active ion uptake, an energy requiring process. Likewise, they may exclude certain ions by actively maintaining an internally negative ionic gradient. These processes are known to occur but are not completely understood. Bioaccumulation information can be found in the ecological effects summaries for individual elements in Section 6.6. Bioaccumulation information specific to edible aquatic organisms is presented in a consolidated fashion in the following subsection.

Bioaccumulation Potential in Aquatic Organisms

Aquatic organisms are the major organismal group where bioaccumulation effects are widespread and quite significant in some cases. The primary reason for large concentration factors in some organisms is the effects of foodchain magnification. For example, arsenic is a known cumulative poison in many organisms. This means simply that these organisms, man for example, can neither effectively excrete nor metabolize arsenic taken into the body. Because of this, residual levels may build up if cumulative trace elements are ingested routinely in the form of contaminated food, water, or air.

Trace element concentrations in seawater, freshwater, and edible aquatic plants, invertebrates, and fish, as well as the concentration factors associated with these organisms are presented in Table 6-3 and 6-4. The concentration factors were derived as representative values for the main classes of edible aquatic organisms (as the edible parts of these organisms, i.e., muscle and soft parts of fish and invertebrates). As such, they can be used for estimating dose to man and other organisms. These values were derived from a wide range of organisms and ecosystems, and only an order of magnitude accuracy for specific cases is suggested. The values presented for concentrations in marine organisms and seawater are representative of estuarine or continental shelf waters only. Since these waters are often high in suspended solids, the reported concentrations are higher than for the open ocean. Finally, the reader should be aware that these concentration factors are based on the uptake of tracer radionuclides by aquatic organisms in laboratory studies, which may not be representative of normal feeding conditions. Again, only an order of magnitude reliability of these values is suggested (48).

6.4 HUMAN HEALTH EFFECTS

Growing concern over the expected rise in trace metal concentration due to increased fossil fuel combustion and its effects on human health is evident in the number of articles devoted to this subject in the recent literature. Current research efforts have not yet determined what the exact effects of chronic, low level trace metal pollution in the atmosphere will be. Most epidemiologic and laboratory studies to date have been concerned with occupational exposure levels found only in industry, and acute responses to trace metal pollutants. Because the concentrations of the trace metals in question are much higher in these cases than what is expected in the environment, extrapolation of acute responses to public health concerns is probably not valid . The effects of synergisms with other trace metals present in the environment is not accounted for in most laboratory or occupational health studies. Also, many elements in question do not have TLV's (Threshold Limit Values) associated with their toxic effects as is the case of carcinogens mentioned in Subsection 6.1.

TABLE 6-3. TRACE ELEMENT CONCENTRATIONS IN FRESH WATER AND FRESH WATER ORGANISMS

Element	(ppm) Concentration In Freshwater	(ppm) Concentration In Freshwater Plants	Concentration Factor	(ppm) Concentration In Freshwater Invertebrates	Concentration Factor	(ppm) Concentration In Freshwater Fish	Concentration Factor
Lithium	5.00E-3	1.50E-2	3.00E0	2.00E-1	4.00E1	2.50E-3	5.00E-1
Beryllium	5.00E-4	1.00E-2	2.00E1	5.00E-3	1.00E1	1.00E-3	2.00E0
Fluorine	1.00E-1	2.00E-1	2.00E0	1.00E1	1.00E2	1.00E0	1.00E1
Sodium	1.00E1	1.00E3	5.00E2*	1.70E2	2.00E2*	2.00E2	1.00E2*
Magnesium	1.00E1	1.00E3	1.00E2	1.00E3	1.00E2	5.00E2	5.00E1
Silicon	4.00E0	5.00E2	1.25E2	1.00E2	2.50E1	1.00E1	2.50E0
Phosphorous	2.00E-2	2.00E2	5.00E5*	2.00E3	2.00E4*	2.00E3	1.00E5*
Chlorine	1.00E1	5.00E2	5.00E1	1.00E2	1.00E2	5.00E2	5.00E1
Calcium	1.50E1	2.00E3	1.33E2	5.00E3	3.33E2	6.00E2	4.00E1
Chromium	5.00E-3	2.00E-1	4.00E3*	1.00E-1	2.00E3*	2.00E-1	2.00E2*
Manganese	1.00E-2	1.00E2	1.00E4*	4.00E2	9.00E4*	1.00E0	4.00E2*
Iron	1.00E-1	1.00E2	1.00E3	3.20E2	1.20E3	1.00E1	1.00E2
Cobalt	5.00E-4	1.00E-1	2.00E2	1.00E-1	2.00E2	1.00E-2	5.00E1*
Nickel	1.00E-2	5.00E-1	5.00E1	1.00E0	1.00E2	1.00E0	1.00E2
Copper	1.00E-2	1.00E1	2.00E3*	1.00E1	4.00E2*	2.00E0	5.00E1*
Zinc	1.00E-2	1.00E1	2.00E4*	1.00E2	1.00E4*	1.00E1	2.00E3*
Arsenic	3.00E-3	5.00E0	3.00E3*	1.00E0	4.00E1*	1.00E0	1.00E2*
Selenium	3.00E-3	3.00E0	1.00E3	5.00E-1	1.67E2	5.00E-1	1.67E2
Silver	1.30E-4	2.60E-2	2.00E2	1.00E-1	7.69E2	3.00E-4	2.31E0
Cadmium	5.00E-4	5.00E-1	1.00E3	1.00E0	2.00E3	1.00E-1	2.00E2
Barium	5.00E-2	2.50E1	5.00E2	1.00E1	2.00E2	2.00E-1	4.00E0
Mercury	1.00E-4	1.00E-1	1.00E3	1.00E1	1.00E5	1.00E-1	1.00E3
Lead	5.00E-3	1.00E0	2.00E2	5.00E-1	1.00E2	1.50E0	1.00E2*

*Concentration Factors are measured, rather than derived values.

Source (48).

TABLE 6-4. TRACE ELEMENT CONCENTRATIONS IN SEAWATER AND MARINE ORGANISMS

Element	(ppm) Concentration In Seawater	(ppm) Concentration In Marine Plants	Concentration Factor	(ppm) Concentration In Marine Invertebrates	Concentration Factor	(ppm) Concentration In Marine Fishes	Concentration Factor
Lithium	2.00E-1	6.00E-1	3.00E0	1.00E-1	5.00E-1	1.00E-1	5.00E-1
Beryllium	5.00E-6	5.00E-3	1.00E3	1.00E-3	2.00E2	1.00E-3	2.00E0
Fluorine	1.40E0	2.00E0	1.43E0	5.00E0	3.57E0	5.00E0	1.00E1
Sodium	1.05E4	1.00E4	9.52E-1	2.00E3	1.90E-1	7.00E2	1.00E2*
Magnesium	1.30E3	1.00E3	7.69E-1	1.00E3	7.69E-1	1.00E3	5.00E1
Silicon	3.00E0	2.00E2	6.57E1	1.00E2	3.33E1	3.00E1	2.50E0
Phosphorous	7.00E-2	2.00E2	3.00E3*	2.00E3	3.00E4*	2.00E3	1.00E5*
Chlorine	7.90E4	6.00E3	7.59E-2	1.50E3	1.90E-2	1.00E3	5.00E1
Calcium	4.00E2	2.00E3	5.00E0	5.00E3	1.25E1	2.00E2	4.00E1
Chromium	5.00E-5	1.00E-1	2.00E3	1.00E-1	2.00E3	2.00E-2	2.00E2*
Manganese	1.00E-3	2.00E1	5.50E3*	1.00E1	4.00E2*	6.00E-1	4.00E2*
Iron	1.00E-2	5.00E2	7.30E2*	2.00E2	2.00E4	3.00E1	1.00E2
Cobalt	1.00E-4	1.00E-1	1.00E3	1.00E-1	1.00E3	1.00E-2	5.00E1*
Nickel	2.00E-3	5.00E-1	2.50E2	5.00E-1	2.50E2	2.00E-1	1.00E2
Copper	3.00E-3	3.00E0	1.00E3	5.00E0	1.67E3	2.00E0	5.00E1*
Zinc	1.00E-2	1.00E1	1.00E3	1.00E3	5.00E4*	2.00E1	2.00E3*
Arsenic	3.00E-3	5.00E0	1.67E3	1.00E0	3.33E2	1.00E0	1.00E2*
Selenium	1.00E-4	1.00E-1	1.00E3	1.00E-1	1.00E3	4.00E-1	1.67E2
Silver	3.00E-4	6.00E-2	2.00E2	1.00E0	3.33E3	1.00E0	2.31E0
Cadmium	1.00E-4	1.00E-1	1.00E3	2.50E1	2.50E5	3.00E-1	2.00E2
Barium	1.00E-2	5.00E0	5.00E2	1.00E0	1.00E2	1.00E-1	4.00E0
Mercury	3.00E-5	3.00E-2	1.00E3	1.00E0	3.33E4	5.00E-2	1.00E3
Lead	1.00E-3	1.00E0	5.00E3*	1.00E0	1.00E3	3.00E-1	1.00E2*

*Concentration factors are measured rather than derived values.

Source: (48)

6.4.1 Effects of Trace Metals Exposure

Weisburger (49) of the National Cancer Institute in Maryland has estimated that 50 to 90 percent of human cancers are caused by carcinogens in the environment. Hamilton and Manne (50) estimated that total production of electric power in the U.S. in 1975 was associated with between 2,000 and 19,000 deaths and 29,000 to 48,000 disabilities. This is roughly between 0.2 and 2 percent of the total deaths in the U.S. for ages 1-74 during this time period. The percent of deaths attributable to trace metal emissions alone was not calculated. Jacobs (3) reviewed literature covering the past 50 years with regard to air pollution and its relationship to pulmonary disease. Besides concluding that a high correlation exists between community air pollution and pulmonary disease, he noted that air pollution affects those most who are least able to stand stress; those over 65 years of age, under 1 year of age, and the sick. Specific air pollution episodes and related mortality increases are discussed.

Chronic air pollution has been studied with regard to occupational health effects. A review of the literature present in this area is beyond the scope of this report, but occupational exposure to coal dust is of obvious interest. Carlberg et al. (51) surveyed British, German, and U.S. data concerning concentrations of trace metals present in bituminous coal miner's lung tissue. Be, Mg, Ti, Va, Cr, Mn, Fe, Ni, Cu, Zn, and Pb concentrations were higher in miners' lung tissue than values reported for non-miners' lungs. Another study of chronic air pollution in an industrial area in Japan (52) indicated a correlation between a smog episode and increased mortality during the period. Particles containing As, F, Pb, Ca, S, V and other pollutants were the probable cause of the increased mortality. Smog in this region most often occurs in the winter, and results of this study showed that school children had lower peak bronchial flow rates in the winter in polluted areas.

Gasper and Dauzvardia (53) performed an assessment of trace element body burdens that would result from projected coal utilization in the Illinois River Basin. The elements examined were As, Be, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Se, V, and Zn. Regional atmospheric concentrations of trace elements resulting from hypothetical year 2020 levels of coal consumption were calculated from estimates of total particulate matter. The assumption was made that trace elements would be present on the particles in concentrations equivalent to: (1) their concentrations in coal, and (2) relative rates of emission. The results concluded that new emissions may lead to a doubling of present trace element body burdens in the area.

Hildebrand (54) is currently conducting research to monitor cellular metabolism and fate of fossil fuel-related pollutants to determine effects of these agents on regulation of gene structure and activity. Results to date include an accumulation of cadmium (to levels 1000-fold greater than in growth media) in mammalian cells cultured in levels of $CdCl_2$ well below toxic levels. Sixty-five to seventy-five percent of the Cd was localized in chromation. Other biochemical studies have documented the teratogenic properties associated with Cd, Se, and Hg, mutagenic properties associated with Pb and Hg, and carcinogenic properties of Be and Se (55).

The food and Drug Administration's Market Basket Survey (56) indicates that total Hg, Pb, and Cd dietary intake are about 7, 14, and 75 percent, respectively, of the WHO/FAO recommended tolerable limits. Elevation of these trace metals in the water, atmosphere, and foodstuffs is thus a matter of concern. Torrey (57) cites evidence that exogenous trace elements are more soluble than endogenous trace elements in soils, and thus more likely to enter the food chain and ultimately affect man.

Shakeman (58) reports that environmental Cd may be important in the development of hypertension. Hickey _et al._ (59) have correlated atmospheric Cd and V concentrations with the incidence of mortality due to diseases of the heart. Finally, synergisms that are associated with SO_2 concentrations and trace metal contaminated particles have been noted (60, 61, 62, 63, 64). These synergisms have resulted in a general increase in the degree of mortality and morbidity for a given air pollution episode.

Acute responses due to trace metal exposure have been noted for a few fly ash extraction laboratory studies. Chrisp *et al.* (65) evaluated the mutagenicity of soluble components of respirable fly ash taken downstream from ESP units at a coal-fired plant. Mutagenic responses of the bacterium *Salmonella typhimurium* were observed. The results were consistent with the hypothesis that both organic and inorganic trace element mutagens are present in coal fly ash. A similar study (66) determined that fly ash caused changes in DNA of *Salmonella typhimurium*. Chemical analysis of fly ash extract detected the presence of 11 metals including Cd, Se, Pb and Be.

6.4.2 Particle Size and Effects

Particle size distribution data for fly ash taken from two coal-fired plants equipped with ESP units is given in Table 6-5. Examination of these data indicates a sizeable percentage (62.5% and 67.8%) of the fly ash emitted from these plants is in the 3.3μm or smaller size range. This size range of particles has the greatest potential for significant inhalation health effects.

TABLE 6-5. PARTICLE SIZE DISTRIBUTION IN FLY ASH

Approximate Size Range, μ	Site A[1] Ash Fraction (%)	Site B[2] Ash Fraction (%)
>8	9.5	15.3
5-8	11.4	6.8
3.3-5.0	16.6	10.1
2.3-3.3	11.6	10.4
1.5-2.3	20.9	16.6
.75-1.50	17.2	21.8
.45-.75	8.6	13.2
.30-.45	2.7	2.5
<.30 + vapors	1.6	3.3
	100.0	100.0

[1] A 350 MW boiler equipped with a hot-sided ESP. Source: 67

[2] A 350 MW boiler equipped with a cold-side ESP.

Trace Metal Concentration with Particle Size

Studies have shown that certain trace elements present in fly ash particles emitted from coal-fired plants exhibit a dependence of element concentration on particle size. Davison et al. (68) determined Pb, Cd, Se, Ar, Ni, Cr, and Zn all show a pronounced increase in concentration with decreasing particle size. Fe, Mn, Si, Mg, and Be show a limited increase in concentration with decreasing particle size. Cu, Co, and Ca show no concentration trends with particle size. Kaakinen et al.(69) measured the amount of 17 elements in inlets and outlets of a coal-fired plant. Concentration of Cu, Zn, As, Sb, Pb, Po, and Se are generally lowest in bottom ash and increase progressively in fly ashes collected downstream toward the stack. Sections 3, 4, and 5 presented various aspects of the dependence of trace metal concentration with particle size. Although only a small fraction of the total fly ash produced has particle diameters <1 μm, the fraction emitted presents a greater potential health hazard per unit weight than that retained. Existing particle control devices are least effective for removing the most toxic particles based on these data. The predominance of certain toxic elements in small particles is also significant in determining the degree of enrichment of these elements in an urban aerosol, since these small particles have the longest atmospheric residence time. Gladney et al. (70) have shown enrichment factors of greater than ten times natural crustal abundance for Cr, Ni, Cu, Zn, As, Cd, Pb, Se, and Cl in the Boston aerosol and have established correlations with enrichment patterns in coal fly ash, municipal incinerator fly ash and residual fuel oil.

Dependence of Deposition and Retention Rates in the Lung on Particle Size

The difficulty of the control problems for hazardous air pollutants is compounded because the degree of toxicity is not simply proportional to the mass emissions. Very small amounts of small particulate material can have severe effects on human health, not only because small diameter particles are more potent, but because they are more easily respirable and more readily retained in the lungs.

Figures 6-2 and 6-3 demonstrate this point. Figure 6-2 shows a substantial increase in the fraction of particles deposited in the pulmonary and tracheobronchial systems with decreasing particle size. The retention of particulate matter in the lung also increases dramatically at particle diameters less than 3 μm (Figure 6-3). The peak retention rate is at approximately 1 μm at which point over 75 percent of the particles deposited are retained. More than half of all particles in the range of 0.5 to 2.0 μm will be retained while only a small amount of those particles less than 0.25 μm or more than 3 μm are retained. Comparison of these data with the particle size data for emitted fly ash particles presented earlier (Table 6-5) indicates that a significant fraction (almost 50 percent) of the particles emitted will have a 50 percent or greater retention rate in the lungs.

Other studies have suggested that the penetrating ability of small particles, which is primarily due to geometric size considerations, is also dependent on lung tidal volume (72). Deposition in a particular pulmonary compartment may not be easily predicted according to particle size alone. Fennelly (73) reports that irritation due to particle deposition can lead to impairment of oxygen transfer and effect a reduction in lung tidal volume. Conversely, another study(74) based on empirical evidence suggests that deposition in the lung may be higher than expected for larger particles.

The smallest particles deposited in the pulmonary region are of the most concern toxicologically for two reasons. These particles have been shown to be enriched in many toxic trace elements, some of which are known carcinogens. Secondly, the efficiency of extraction of toxic species from particles deposited in the pulmonary region is high (60 to 80 percent) (68) due to their long residence times and their larger surface area. The extraction efficiency for larger particles deposited in the tracheobronchial and nasopharyngeal regions is low (5 to 15 percent). Particles deposited in these regions have short residence times due to their removal by cilial action to the pharynx where they are either swallowed or expelled. Consequently, toxic species that predominate in the submicron-sized particles will have their entry into the bloodstream enhanced over those species that predominate in larger particles (68). Also, smaller particles cause greater

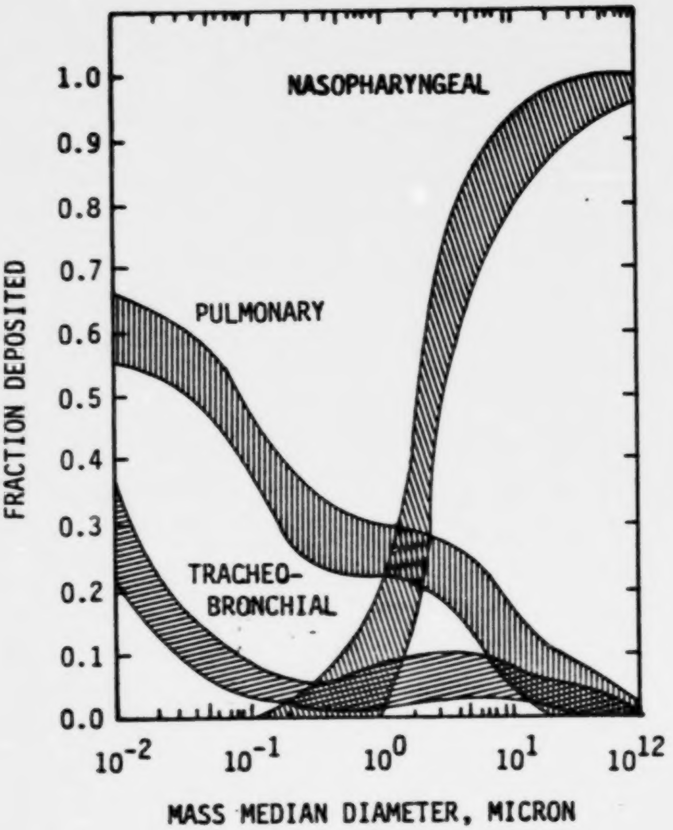

Figure 6-2. Fraction of particles deposited in the three respiratory trace compartments as a function of particle diameter.

SOURCE: (71)

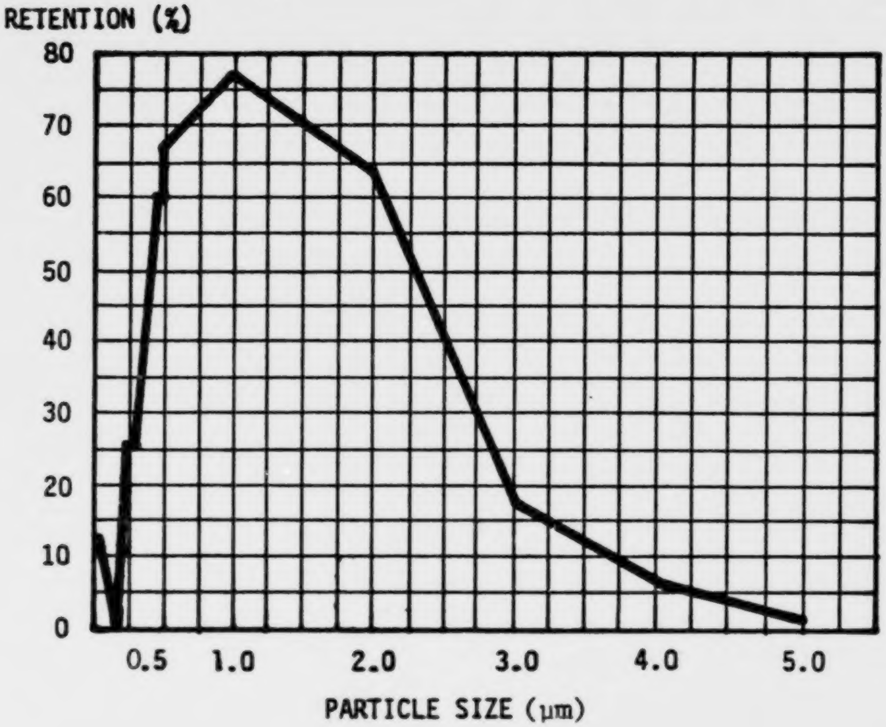

Figure 6-3. Retention of particulate matter in lung relation to particle size.

SOURCE: (71)

irritation (75). Other studies (76) support these findings by demonstrating that the number of free macrophages present in the lung increases when smaller particle sizes are present.

The consequences of short- and long-term increases in toxic trace element body burdens can be quite severe. Investigators at U.C. Davis have reported that, based on the Ames Test, a cyclohexane extract of the finest fly ash particles from a coal-fired plant was mutagenic. Further, mutagenic activity increased with decreasing particle size (77). Among the specific consequences of long term, low level exposure to highly toxic trace elements are increased incidences of disease and reduced life spans in the affected human population (71).

6.4.3 Safe Ambient Trace Metal Concentrations

Most research pertaining to safe ambient trace metal concentrations is taken from an occupational health perspective. Toxicity studies based on threshold limit values have been suggested as a possible method of assessing trace metal hazard levels in the environment. Threshold limit value (TLV) is the time-weighted concentration of a substance that a healthy worker can be exposed to for a 7 or 8 hour workday and a 40 hour work week without known deleterious effects. One author (78) has suggested that TLV values be used in order to estimate permissible concentrations in the environment at large for specific elements. Using this approach, elements in question are first assigned some toxicity potential rating, and the TLV for a particular element (or one of equivalent toxicity if no TLV for that element has been proposed) is divided by some arbitrary safety factor to arrive at an estimated safe concentration in the environment.

Several problems are apparent in this approach. Occupational toxicology studies do not include the potential for contamination of food and water as well as the atmosphere in their scope. Bioaccumulation and/or other concentration effects may be very significant when the cumulative effects of increased reliance on coal combustion are felt in the future.

The potential for significant synergisms is also not accounted for in an approach based on TLV data for individual elements alone. Fine particles contain a full spectrum of trace metals on their surface when emitted from a coal-fired plant. These trace metals have a potential for interactive reactions which could result in more serious health effects than when individual element concentrations are considered alone.

In spite of the limitations inherent in any attempt to assign a value to safe concentration levels in the environment, data on Estimated Permissible Concentrations (EPC) is presented in Table 6-6. This information was extracted from The Multimedia Environmental Goals for Environmental Assessment (79). These values are based on toxicity data from a number of sources: TLVs, NIOSH recommendations, and/or lethal dose to some animal. The reader should not interpret this information as an established standard, but rather as the best estimate available for acceptable ambient level concentration of certain trace elements in the environment; see Section 9.

The best hope for obtaining reliable estimates of safe ambient trace metal concentrations (including contributions from anthropogenic sources) would seem to be a multi-pollutant and multilocality interdisciplinary epidemiological study. Noyman (80) has suggested an apporach such as this, since extrapolation from present findings is difficult and unvalidated.

6.4.4 Dosage-Response Relationships

Very little data on human health dosage-response characteristics are available. Most attempts to date to quantify the health impacts of trace metal emissions from a specific source have estimated total body burden increases to assess the effects. Generally speaking, increased combustion of fossil fuel is expected to increase the respiratory and dietary exposure of trace elements in the population (81).

One study (53) investigated projected increases in trace element body burdens due to coal utilization in the Illinois River Basin in the future. Principal routes of exposure were assumed to be absorption within the respiratory tract through inhalation and absorption in the gastrointestinal tract through ingestion of contaminated food and water. Standard Reference Man. (International Conference on Radiation Protection) was used to estimate body burden increases: 20 m^3 air inhaled per day, 2 ℓ water ingested per

TABLE 6-6. TOXICITY-BASED ESTIMATED PERMISSIBLE CONCENTRATIONS

Compound	Air µg/m^3 Health	Air µg/m^3 Ecology	Water µg/ℓ Health	Water µg/ℓ Ecology	Land µg/g Health	Land µg/g Ecology
Ag	0.024				0.10	0.01
Al	12.6		73		0.15	0.40
As	0.005				0.10	0.02
B	7.4		43		0.09	10.00
Ba	1.0				2.00	1.00
Be	0.8		4		0.008	0.02
Cd	0.12				0.02	0.0004
Co	0.12		0.7		0.000	0.1
Cr	0.12				0.1	0.1
Cu	0.5				2.0	0.2
Ge	1.3		8.0		0.016	
Hg	0.1	1.0			0.004	0.1
Li	0.05		0.3		0.0006	0.15
Mg	14.0		83.0	43,300	0.2	87.0
Mn	12.0				0.1	0.04
Ni	0.24		1.4		0.003	0.004
P	0.24		1.4		0.003	0.0002
Pb	0.36				0.1	0.02
Se	0.5				0.02	0.01
Sr	3.5		27.0		0.05	
Ti	14		83	4,100	0.17	8.0
V	1.2	0.1	7		0.014	0.15
Zn	9.5				10.0	0.04

Source: (79)

day, and a 70 kg body weight. Results of this study indicated that except for Hg and V, dietary contribution to the total body burden level for the elements in question never falls below 66 percent and averages 87 percent. They predicted a doubling of trace element body burdens and assumed that the human health effects would be related to body burden levels.

Dosage-response information for acute levels of exposure are presented in the individual health and environmental summaries for specific elements in Section 6.6. These data are primarily from laboratory studies (LD 50, LC 50, etc.) on test animals and may only be of limited usefulness for assessing large-scale human health and environmental effects.

6.5 RESEARCH NEEDS

Many data and information gaps have been identified in this section. Specific research needs are discussed briefly.

A general need exists to increase the extent of baseline monitoring around SCCP's. Evaluation of impacts to the environment requires a more thorough understanding of baseline conditions than is currently present. Research in this area should also attempt to elucidate environmental transport processes, and determine some basic understanding on how and where cycling of anthropogenic trace metals occurs. Field data are needed on biological uptake and bioaccumulation processes.

Epidemiological studies of chronic, low level exposure to trace metals are needed. Emphasis should be placed on possible synergistic responses with other trace metals, and non-trace metal pollutants present as well. In order to accomplish this in a meaningful fashion, more information about the specific physiochemical forms of emitted trace metals is needed. With this information realistic biochemical studies can begin to determine specific health effects of these pollutants at a cellular level.

Finally, more research is needed on effective control methods to limit trace metal emissions at the source. Most of the problems center around very fine particulate emissions which are highly enriched in toxic trace metals, but some gaseous emissions (i.e., Hg and Se) are of concern as well. A discussion of this subject material is presented in Section 4.

6.6 SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS LITERATURE

Table 6-7 summarizes existing ecological and health information for a number of trace elements. The information presented was extracted from two government publications; HASL-320 by Merrill Heit of the Health and Safety Laboratory of the U.S. EPA, New York (82), and Multimedia Environmental Goals for Environmental Assessment, Vol. II by Cleland and Kingsbury of Research Triangle Institute, RTP, North Carolina (70). Original references are included for completeness. This subsection is intended to provide the reader with a quick, general summary of known ecological and health effects information in order to augment the specific studies referenced earlier in this section.

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Aluminum (Al)		Although aluminum is not a highly toxic element, large quantities may produce deleterious effects, such as pulmonary fibrosis from inhalation of aluminum powder (83). Only massive oral doses of aluminum are reported to be toxic to mammals (84).	A level of 4,000 mg/kg in diet caused phosphorus toxicity; a concentration of 0.07 mg/ℓ aluminum nitrate, as Al, is toxic to stickleback (Gasterosteus aculeatus). Aluminum is reported to be concentrated 10,000 times in fish muscle, and 15,000 times in benthic algae. Aluminum compounds may adversely affect benthic organisms (e.g., clams, crabs, oysters, lobsters) (85). High concentrations of aluminum in soils with low pH causes restricted root growth in plants (86). Growth reductions in wheat and orange seedlings were reported in nutrient solutions with 0.1 mg/ℓ of aluminum (85). Aluminum is toxic to plants in acid soils; however, at pH values between 5.5 and 8.0 soils precipitate soluble aluminum so as to eliminate its toxicity (87).
Antimony (Sb)	The relative order of toxicity, imtraperitoneally, of antimony compounds beginning with the most toxic is; metallic antimony, antimony trisulfide, antimony pentasulfide, antimony trioxide, and antimony pentoxide (88).	Effects of intoxication may include skin irritation, inflammation of mucous membranes and nervous system and gastointestinal effects. Chronic poisoning may result from inhalation of antimony or its compounds. The lowest toxic concentration reported for human is 4,700 μg/m^3 for 20 weeks. Antimony is slowly absorbed from the gastrointestinal tract in man. Trivalent forms of antimony concentrate in the red blood cells and the liver, and are slowly excreted, primarily in the feces. Pentavalent forms of antimony accumulate mainly in the blood	Little is known of the ecological effects of antimony. However, antimony may be concentrated by some marine organisms to levels above that present in seawater (89). LD_{50} (oral, rat): 100 mg/kg for antimony. Toxicity to aquatic life: The 96 hr LO_{50} for fathead minnow is 80 ppm (antimony trioxide). This is equivalent to 67 ppm at SB. Antimony can be concentrated by various marine forms to over 300 times the amount present in seawater (85). Concentrations as low as 1 mg/ , as Sb, have produced effects in fish (90).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Antimony contd.		plasma, liver and spleen, and are primarily released through the urine. It appears that antimony will not accumulate in man over long time periods. If heavy exposure does occur, symptoms similar to those of arsenic poisoning may result (84). Chronic effects of antimony uptake in man are unknown. Some investigators have suggested a relationship between antimony and pulmonary carcinogenesis based on a possible antimony containing abnormal enzyme system (84).	
Arsenic (As)	Compounds may be absorbed by inhalation, ingestion, and through the skin. Excretion is slow: 10 days for acute absorption > 1 year for prolonged exposure (91). Cumulative poison (88).	(Arsenic): The toxicity of arsenic to humans depends upon its chemical form. Organic arsenic compounds are considerably more toxic than the inorganic forms which occur in living tissues or are used as feed additives. Differences in toxicities of various forms are clearly related to their rates of excretion, the least toxic being the most rapidly eliminated (92). Arsenic has been shown to accumulate in the body faster than it is excreted. It can build to toxic proportions from small amounts absorbed from periodic exposure or dietary contamination (93). Arsenate is excreted rapidly from the kidneys and probably does not accumulate in humans. Arsenites accumulate in the liver, muscle, hair, nails and skin. Intake of arsenic by man has been	Arsenic is ubiquitous in the environment, occurring in various forms. Trivalent arsenic compounds (arsenite) are, in general, more toxic than pentavalent compounds (arsenate). In nature, the arsenate compounds are more prevalent than the arsenite compounds. Arsenic may also be methylated by microorganisms. Arsenic occurs primarily in the pentavalent form in the soil (95). The formation of arsenic compounds is affected by acidity and the Fe, Al, Ca, P and humus content of the soil. Soils with high reactive aluminum levels have been found to be less phytotoxic even after heavy applications of arsenic (96). Arsenic toxicity has been observed in plants growing on soils treated with arsenical pesticides, herbicides and defoliants.

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Arsenic (contd.)		implicated in skin and respiratory cancer (84). Most arsenic is ingested by humans in fish, meat and poultry (56%), dairy products (23%), grain and cereal (14%), and potatoes (6%) (94). Arsenic poisoning has caused dermatitis, pharyngitis, conjunctivitis, and perforation of the nasal septum (88). LD_{LO} (intramuscular, rat): 25 mg/kg.	These plants were found to contain relatively low levels of arsenic probably due to its action as a metabolic inhibitor (97). When present in soils, toxic amounts of arsenic arrest the germination of seeds and reduce the viability of seedlings, In addition, the rate of nitrification in the presence of arsenic in soils is decreased (96). Arsenic is a cumulative poison with long term chronic effects on both aquatic organisms and on mammalian species. There is some evidence that arsenic is concentrated in aquatic food chains, often reaching concentrations in excess of proposed EPA standards (98). There is little information on the accumulation of arsenic in freshwater organisms. Some species of freshwater fish, have been reported to concentrate arsenic by a factor of 20 to 130 above the concentration in water (99). The freshwater invertebrates Daphnia sp and crayfishes have also been reported to concentrate arsenic (100). Arsenic is accumulated by many marine fauna. Marine algae have also been reported to concentrate arsenic (97). Arsenic also tends to be accumulated by oysters and other marine shellfish where concentrations of up to 100μg/g have been reported (101).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Arsenic (contd.)			Toxicity to sensitive plants varies from 110-340 kg/ha for sandy to clayey soils (85). Concentration of 0.5 mg/ℓ in nutrient solutions is toxic to pineapple and orange seedlings and reduces tomato yield 80% (102). Concentrations of 1.1-2.2 mg/ℓ are toxic to pike perch (Stizostedion vitreum) (85).
Barium (Ba)	Barium is readily excreted and is probably noncumulative (102).	Of the barium which is ingested, only a small amount is retained in mammals for periods greater than 24 hours. Very low concentrations have been found in the mammalian kidney, spleen, skeletal muscle, heart, brain, liver and skeleton (84). The toxicity of barium to mammals depends upon the chemical species. Insoluble forms of barium, such as barium sulfate, are not toxic whereas soluble barium compounds are highly toxic. The lethal dose to humans is considered to be between 0.8 and 0.9 gram of barium chloride. At present there are no studies revealing how much barium is tolerable in drinking water nor have any studies been made of the long term effects of the consumption of barium (87). Soluble barium compounds are highly toxic when ingested. Insoluble barium compounds are generally nontoxic (103). Fatal dose for humans is 0.55-0.60 g as Ba (104) stimulates all muscle types, causes vasoconstriction, and initially stimulates and then paralyzes the central nervous system. BaO and $BaCO_3$	Barium is relatively common in nature and occurs in plant and animal tissues (84). Plants have been shown to accumulate barium from soil (84). All water and acid soluble barium compounds are reported to be poisonous. However, the sulfate and carbonate present in seawater precipitate barium and thus tend to mitigate its effects on marine life (87). Some concentration factors from seawater for barium have been reported as 17,000 for phytoplankton, 900 for zooplankton, and 8 for fish muscle (87,101). An accumulation of radioactive barium in the internal organs, gills and scales of fish from the northwest Pacific has also been reported (87,106). LC_{50} for snail Planorbis glabratus is reported as 11 ppm, time unspecified, for toxic effects (85). 500 ppm barium nitrate (as Ba) is toxic to Stickleback (87). Ba can be concentrated in goldfish by a factor of 150 (85).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element.	General Information	Human Health Effects	Ecological Health Effects
Barium (contd)		have caused respiratory injury in man LD_{LO}(oral rat): 335 mg/kg as $BaCl_2$ (or 220 mg/kg as Ba). Teratogenic effects: 20 mg of $BaCl_2$ injected into chick yolks produced curled toes in about 50 percent of survivors (105). TD_{LO} = 878 mg/kg, as Ba.	
Beryllium (Be)	Toxic through all routes of absorption. Major hazard to health is through inhalation. Particle size of beryllium dust critical factor in causing berylliosis (107).	Chronic exposure to soluble as well as insoluble compounds as particulates in air results in berylliosis, a severe lung disease. Lowest reported toxic concentrations for humans is .1 mg/m^3 (108). LD_{50} (oral, rat) equivalent to 9.7 mg/kg for Be. Minimum dosage producing carcinogenic response is equivalent to absorption by inhalation of 0.4 μg/kg (108,109). Beryllium is not well absorbed when given to humans by any route. After inhalation, beryllium is retained in the lungs and is mobilized slowly. The beryllium which is absorbed by the body is mostly excreted in the urine (84). In humans, beryllium has been shown to produce many effects depending upon the dose and duration of exposure. The most extensive changes usually occur in the lungs (84). At present, it is not clear if exposure to beryllium compounds is associated with an increase in the incidence of carcinomas in humans (110). The salts of beryllium are not highly toxic for intake by ingestion since laboratory rats survived for two years on a diet containing beryllium at a concentration of 18 mg/kg body weight daily (87).	The addition of beryllium to soil has been shown to have some effects on plant growth. For example, some varieties of citrus fruit seedlings show toxic effects at concentrations of 2.5 to 5 μg/l beryllium (111). In addition, beryllium has been shown to inhibit photosynthesis and growth in some crop plants (112-114). However, it is unknown if the same effect occurs in marine flora where is has been reported to be concentrated by a factor of 1,000 (84,115). Toxic concentration for fathead minnow, 96 hr. LC_{50}, is 0.15 mg/ℓ as $BeCl_2$ in soft water (85). Can be concentrated 1,000 times in marine organisms (102). Growth of bush beans reduced by 0.5 mg/ℓ in nutrient solution (85).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Bismuth	Bismuth is considered as one of the less toxic of the heavy metals.	It causes kidney and liver damage only when ingested in large doses (116). It behaves similarly to lead in the body (83).	Little is known of the effects of bismuth on either terrestrial or aquatic systems. Concentrations of 0.04 to 0.3 mg/l have been reported for marine animals, indicating concentration factors up to 10,000 (87,115). Bismuth has a fairly low level of toxicity to mammals. It causes kidney and liver damage only when ingested in large doses (116). LD_{50} for dihydroxypropoxy bismuth (intravenous, rat): 13 mg/kg; molecular wt, dihydroxypropoxy bismuth: 302. (as BI): 209/302 x 13 = mg/kg (based on LD_{50} for dihydroxypropoxy bismuth).
Boron (B)	Boron is not a highly toxic element.	In humans, practically all of the boron is absorbed from food and excreted via the kidneys. It has been reported that concentrations as high as 30 mg/l of water are not harmful to man (117). It does not accumulate significantly in body tissues (85). Serious effects to humans are not reported for reasonable exposures.	Boron occurs regularly in natural water supplies and in plant and animal tissues. It is an essential nutrient to plants, but not to animals. While essential for growth at higher concentrations, boron is very toxic to many terrestrial plants and produces adverse effects at concentrations exceeding 1.0 mg/l of water (87). Available data on toxicity of born to aquatic organisms are mostly from freshwater. Since the toxicity of boron is slightly lower in hard water than in distilled water, it is anticipated that boric acid and borates would be less toxic to marine aquatic life than to freshwater organisms (87). The effects of boron on marine vegetation are unknown (87).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Boron (contd)			Boron has a low order of toxicity to livestock with no evidence of accumulation in mammalian tissues (87). However, in lambs, gastrointestinal and pulmonary disorders have been reported as a result of grazing on vegetation growing in areas of high boron soil content (84). The ingestion of 16 to 20 grams of boric acid per day for 40 days produced no ill effects in dairy cows (87). LD_{50} (oral, mouse): 2,000 mg/kg. Aquatic toxicity: Boron is mildly toxic to fish. The 96-hr LC_{50} for Gambusia affinis (topminnow) is reported as 3,6000 mg/ℓ for sodium borate. There is no evidence that boron is cumulative. Phytotoxicity: Sensitive crops such as citrus show toxic effects from 0.5 to 0.75 mg/ℓ of boron in irrigation water (85).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element.	General Information	Human Health Effects	Ecological Health Effects
Cadmium (cd)	A dangerous, highly toxic, cumulative poison. Does not occur in organic compounds as does Hg or Pb. Zinc and copper increase toxocity.	Cadmium is stated to be an extremely dangerous cumulative toxicant causing insidious, progressive chronic poisoning in mammals, fish and probably other animals, because the metal is excreted at a very low rate (87). In mammals, approximately 6 to 10% of the ingested cadmium is absorbed and transported through the body by red blood cells. Cadmium collects in the kidney, liver, pancreas and blood vessels. Some cadmium is absorbed from the lungs following inhalation. The amount of cadmium uptake from material in the lungs depends on the concentration, particle size, solubility of the particulate matter and physiological considerations. However, under normal conditions, inhalation does not contribute significantly to intake. Most cadmium salts have a short retention time in the lungs (84,118). The kidney has been the initial target organ of retained cadmium. Some symptoms of cadmium poisoning can be prevented by the presence of zinc, selenium cobalt, estrogens and cysteine (84). Most cadmium enters the human diet from grains and cereals(23%), fruits 18%), potatoes (18%) beverages (13%), dairy products (8%), and meat, fish and poultry (5%) (94). Cadmium may enter the body via the gastrointestinal tract from ingestion of fish from polluted waters. When ingested at very high concentrations, it may cause	Cadmium is stated to be "an extremely dangerous cumulative toxicant causing insidious, progressive chronic poisoning in mammals, fish and probably other animals, because the metal is excreted at a very low rate" (87). Cadmium is always found in association with zinc in the earth's crust (123). Cadmium does not degrade in the environment but rather accumulates in soils and sediments where is may enter various food chains (110). When present in soils cadmium is apparently readily taken up by a great number of plant species especially the grasses and grains (e.g., wheat, corn, rice, oats and millet (124,125). Cadmium is also found in peas, beets, lettuce and radishes. The concentration of cadmium reported to be present in an average background soil is 0.55 μg/g Cd and the plants growing in this soil had an average of 0.35 μg/g Cd (26). Yields of some crop plants may be reduced up to 25% by the addition of cadmium to nutrient solutions at concentrations greater than 100 μg/1 (87). The mechanisms by which cadmium is taken up by plants is still largely unknown (126). In addition, there is a lack of information on the behavior of cadmium in terrestrial ecosystems and is transport through food chains. In freshwater systems, floating aquatic plants have been found to accumulate cadmium from

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS.

Element.	General Information	Human Health Effects	Ecological Health Effects
Cadmium (contd.)		itai itai (ouch ouch) disease as reported in Toyama Bay, Japan (119). Cadmium, as has been reported for mercury, may form organic compounds in aquatic systems which may be highly toxic or lead to mutagenic or teratogenic effects when ingested (87). Inhalation or ingestion produces acute and chronic effects. Inhalation of 0.01-0.27 mg/m^3 resulted in pulmonary and renal effects for exposed workers (88). Ingestion of 13-15 ppm has been toxic to children (104). Maximum normal body burden 20-30 mg. (120). Minimum detectable health effects have been theoretically associated with long-term (25-30 years) exposure to air concentrations of 2.5 mg/m^3 (121). LD$_{50}$ (oral rat) equivalent to 6.3 mg as Cd. Occupational exposure reported to increase cancer risk (122). Oncogenic response minimum in an animal is 1 mg/kg, as Cd. Teratogenic response minimum in an animal is 1 mg/kg, as Cd.	concentrations as low as 0.01 μg/g. Although this results in inhibited growth, the concentrations of the metal which accumulated in the leaves and fronds was up to 82 μg/g or a concentration factor of 8200 (127). Little data is available on the cadmium content of marine and freshwater fish, but it does concentrate in the liver (128,129). Of these few aquatic organisms studied for cadmium uptake, mollusks received most of the attention (130,131). The mollusks accumulate their cadmium in calcareous tissues and in the viscera. Concentration factors of 1,000 for cadmium have been reported in fish muscle, as have a concentration factors of 3,000 in marine plants and up to 30,000 in some marine animals (87). Cadmium is also known to have marked acute and chronic effects on aquatic organisms. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, while crustaceans appear to be more sensitive than fish eggs and larvae (123). Cadmium is particularly toxic to gill-bearing marine and freshwater crustaceans and may induce ultrastructural changes in the gills (132). In mammals, approximately 6 to 10% of the ingested cadmium is absorbed and transported through the body by red blood cells. Cadmium collects in the kidney, liver, pancreas and blood vessels. Some cadmium is absorbed from the lungs following inhalation.

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS.

Element.	General Information	Human Health Effects	Ecological Health Effects
Cadmium (contd.)			The amount of cadmium uptake from material in the lungs depends on the concentration, particle size, solubility of the particulate matter and physiological considerations. However, under normal conditions, inhalation does not contribute significantly to intake. Most cadmium salts have a short retention time in the lungs (84,118). Acute lethal concentration for most freshwater fish varies from 0.01 to 10 mg/ℓ (133). Reduced reproduction of Daphnia magna at 0.0005 mg/ℓ. Seven day LD_{50} for rainbow trout (Salmo gairdneri) is 0.008-0.010 ppm. Oysters may concentrate cadmium. Certain plants may take up Cd from soil (121). Yields of beans, turnips, and beets reduced by 0.10 mg/ℓ in nutrient solution (85).
Chromium (cr)	All chromium compounds considered poisonous.	Chromium is only biologically important in the tri- and hexavalent states. In mammals, there is a conversion of hexavalent to trivalent chromium. Trivalent chromium is postulated to be an essential element to mammals (84). Even in its most soluble forms, chromium is not absorbed by mammals and is largely excreted in the feces (134,87).	The concentration of chromium in soils varies greatly; however, the soil chemistry of chromium is largely unknown (138). In some agricultural crops, high levels of chromium can cause reduced growth or death of the crops, whereas adverse effects of low concentrations of chromium on corn, tobacco and sugar beets have also been documented (132). The oxides of

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Chromium (contd.)		Also, it does not appear to concentrate in any particular mammalian tissues or to increase in these tissues with age (87,135). Most human exposure to chromium occurs via intake of food and water. However, the presence of chromium in these substances has not produced any significant adverse effects in either man or experimental animals (84). It should be noted that chromium passes through the placenta and enters the fetus, where it is selectively concentrated in the lung tissue. There is also the possibility of occupationally induced lung cancer due to the inhalation of hexavalent chromium (84,136). Exposure to chromium in air results in injury to nasal tissues. At high concentrations, cancer of the respiratory trace has resulted (88). Pulmonary effects reported with inhalation of 4,500 $\mu g/m^3$ Cr for 5 years (108). LD_{50} (oral, rat): 1,870 mg/kg for $CrCl_3$, equivalent to 615 mg/kg for Cr^{3+}. Cancer has resulted from exposure to 110 $\mu g/m^3$ of CrO_3 (137). Lowest dosage resulting in carcinogenic response is 1 mg/kg.	chromium in the soil are very insoluble and generally unavailable to plants. As with other metals, the toxicity of chromium salts for aquatic life varies with the species, temperature, pH, valence, and the presence of synergistic and antagonistic substances (87). Chromium toxicity is especially sensitive to water hardness (134). Fish are relatively tolerant to chromium salts, but lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae. The reported lethal limits of hexavalent chromium for fish are 17 and 17 mg/l as compared to 0.05 mg/l for macroinvertebrates and 0.032 to 6.4 mg/l for algae (87). Chromium is only biologically important in the tri- and hexavalent states. In mammals, there is a conversion of hexavalent to trivalent chromium. Trivalent chromium is postulated to be an essential element to mammals (84). Even in its most soluble forms, chromium is not absorbed by mammals and is largely excreted in the feces (134,87). Also, it does not appear to concentrate in any particular mammalian tissues or to increase in these tissues with age (87,135). Toxic to aquatic life. Oysters most sensitive to effects: 10-12 μg/ℓ may be lethal.

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Chromium (contd.)			Exhibits a biocumulative effect in aquatic organisms. Some phytoplankton can accumulate chromium 2,300 times the concentration in water. Soybean yields reduced by concentrations of 0.5 mg/ℓ in water solutions and 10 mg/kg in soil cultures (85).
Cobalt (Co)	Cobalt and its salts are cumulative poisons.	In man, cobalt salts are well absorbed by the small intestine. However, significant retention of cobalt by humans does not occur. Approximately 80% of the ingested cobalt is excreted in urine and 15% is removed in the feces Exposure to cobalt and its compounds has resulted in some pulmonary effects, an allergic-type dermititis, digestive changes, and liver and kidney damage (88,83) LD_{LO} (oral, rat): 1,500 mg/kg, for cobalt. LD_{50} (oral, rat): equivalent to 36 mg/kg as Co^{+2}. Ingestion of 1,500 mg/kg of $CoCl_2$ has caused the death of a child. Oncogenic effects minimum TD_{LO} is 2.5 mg/kg of Co (108).	Cobalt has been reported to increase in concentration in the soil around coal-fired power plant from 2.3 µg/g in background soil to 4.6 µg/g in enriched soils near the plant (26). Cobalt is an essential element for both plants and animals. In mammals it is required for activation of vitamin B_{12} (84). The difference between nutritional requirements and toxic dosage in plants may be very small. A concentration of 0.1 mg/l of cobalt in nutrient solutions in irrigation waters is near the threshold toxicity level of plants, whereas a concentration of 0.05 mg/l appears to be satisfactory for continuous application on all soils (139). For wildlife and domestic animals, such as sheep and cattle, a wide margin of safety (a factor of 100) exists between the required and toxic levels (87). the slow accumulation of cobalt, at a concentration of 1 µg/g, over a period of time as short as a month, results in

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Cobalt (contd)			cardiomyopathy (symptoms similar to congestive heart failure) in laboratory organisms (84). Growth of carp (Cyprinus carpio) inhibited by 0.05 mg/ℓ. Growth in Chlorella (algae) and Euglena retarded by 0.04 mg/ℓ. Cumulative in several aquatic species. At 0.1 mg/ℓ, toxic to tomato plants (85).
Copper (Cu)	Concentration of calcium and magnesium influence toxicity of copper in water.	Even when man is exposed to excessive concentrations of copper, chronic symptoms do not result (84). For humans, the only limiting factor of copper in domestic water supplies is taste (87). In form of salts, may irritate gastro-intestinal tract if ingested. Chronic exposure may result in anemia. Exposure to metallic copper fumes may cause respiratory, eye, and skin irratations (88,83). LD_{50} (intraperitoneal, mouse): 3,500 µg/ℓ. LD_{50} (oral, rat): equivalent to 66 mg/kg as Cu^{+2}.	Copper is an essential element for most organisms. However, it can be strongly toxic to plants and aquatic organisms even at very low concentrations when present in its ionic form (140, 141). In general, copper concentrations less than 1 mg/l have been reported to be toxic to many kinds of fish, crustaceans, molluscs, insects, phytoplankton and zooplankton The toxicity of copper varies among organisms. For example, diatoms, dinoflagellates and blue green algae are reported to be more sensitive than green algae to poisoning by copper (40): Thus the enrichment of copper to an aquatic ecosystem would be expected to result in a reduction in primary productivity and the standing crop of many species of phytoplankton. The toxicity of copper to aquatic organisms is also affected

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Copper (contd)			by the physical and chemical characteristics of the water including temperature, hardness, turbidity, and carbon dioxide content. In hard water, the toxicity of copper salts is reduced by the precipitation of copper carbonate or other insoluble compounds (134). Also, the sulfates of copper and zinc, and of copper and cadmium, are synergistic in their toxic effect on fish (87). Copper is accumulated by many marine organisms, with concentration factors of 30,000 reported in phytoplankton, 5,000 in the noncalcareous tissues of molluscs and 1,000 in fish muscle. It is also concentrated in many aquatic invertebrates in which the copper is attached to their blood protein hemocyanin which serves as an oxygen carrier (134,87,101). 96-hour LC_{50} for fathead minnow (*Piephales promelas*) it 0.05 ppm for $CuSo_4$ in soft water, 1.5 ppm in hard water. Inhibits photosynthesis of giant kelp at 0.06 mg/ℓ. Toxic to oysters at 0.1 mg/ℓ. Concentration factor of 30,000 in marine phytoplankton and of 1,000 in marine fish. Concentrations of 0.1-1.0 mg/ℓ in nutrient solutions are toxic to a number of plants (85).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Fluorine (F)		In vertebrates, fluoride is stored primarily in the skeletal tissue. Data from field studies on the levels and bioaccumulation of fluoride show that a level of 2.0 mg/ℓ in livestock drinking water may result in some tooth mottling. This concentration is not excessive from the standpoint of animal health or the deposition of fluoride in meat, milk or eggs. Chronic fluoride poisoning of livestock has been observed when water contained 10 to 15 mg/ℓof fluoride (142). Concentrations of 30 to 50 mg/l of fluoride in the total ration of dairy cows is considered by the EPA to be the upper safe limit (87). Fluoride is transferred only to a very small extent into the milk and to a somewhat greater extent into eggs (87). However, fluoride uptake in ruminants can lead to prenatal skeletal defects. The presence of aluminum may mitigate the effect of fluorosis and it should be noted that aluminum comprises a farily large portion of coal ash. Fluoride may be transformed by some organisms in the natural environment into far more toxic organic fluorides. If this transformation occurs to any significant degree, it could have profound ecological effects (143).	Most studies of fluorine in the environment have been on its effects on food crops. It has been shown the airborne fluoride can damage either the foliage or the fruit of a wide range of plants. Citrus trees, apricot, cherry, plum, grape. Douglas fir and many species of pine, corn, sorghum, and ornamental flowers, in particular, are extremely susceptible to fluoride damage (144). As a result of fluoride pollution and its entry into food chains by accumulation in forage crops, extensive damage to grazing livestock has occurred. Some plant varieties have been found to build up fluoride concentrations in their tissue to levels that are millions of times that found in the surrounding air (144). In contrast to terrestrial studies, data from field studies on bioaccumulation of fluoride in aquatic organisms are virtually nonexistent. However, it is know that fluoride is taken up by some aquatic plants and is stored in the skeletons of fish (143). In vertebrates, fluoride is stored primarily in the skeletal tissue. Data from field studies on the levels and bioaccumulation of fluoride show that a level of 2.0 mg/l in livestock drinking water may result in some tooth mottling. This concentration is not excessive from the standpoint of animal health or the deposition of fluoride in meat, milk or

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Fluorine (contd.)			eggs. Chronic fluoride poisoning of livestock has been observed when water contained 10 to 15 mg/l of fluoride (142). Concentrations of 30 to 50 mg/l of fluoride in the total ration of dairy cows is considered by the EPA to be the upper safe limit (87). Fluoride is transferred only to a very small extent into the milk and to a some what greater extent into eggs (87). However, fluoride uptake in ruminants can lead to prenatal skeletal defects. The presence of aluminum may mitigate the effect of fluorosis and it should be noted that aluminum comprises a fairly large portion of coal ash. Fluoride may be transformed by some organisms in the natural environment into far more toxic organic fluorides. If this transformation occurs to any significant degree, it could have profound ecological effects (143).
Gallium (Ga)		There are no reported adverse effects of gallium in humans following industrial exposure. Gallium is not readily absorbed by mammals from the oral route (84). In humans, gallium has caused metallic taste, skin rashes, and bone marrow depression (145).	Little is known of the toxicity of gallium to either plants or animals. Gallium is not readily absorbed by mammals from the oral route (84). LD_{LO} (subcutaneous, rat): 110 mg/kg for gallium. Gallium compounds generally have a low order of toxicity. Intravenous injections up to 15 mg/kg body weight are tolerated without harm by experimental animals; however, larger doses produce

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Gallium (contd.)			hemorrhagic nephritis. Gallium is slowly eliminated from the body of animals after injection of soluble gallium salts. It is similar to the tissue distribution of bismuth and mercury in the body (145).
Germanium (Ge)	Germanium compounds are generally of a low order of toxicity. They are thought to resemble other organometals, which are usually more toxic than inorganic forms. Animal studies indicate that germanium after absorption is widely distributed throughout the body and is not selectively retained in any tissue (104).	The toxicity of germanium and its compounds is low to mammals even when present at very high levels. Inhalation exposure of rats to germanium and germanium oxide results in rapid clearance from their bodies (84).	The toxicity of germanium and its compounds is low to mammals even when present at very high levels. Inhalation exposure of rats to germanium and germanium oxide results in rapid clearance from their bodies (84). At high exposure levels germanium disturbs the water balance in mammals leading to dehydration, hemoconcentration, fall in blood pressure, and hypothermia (104). Germanium hydride is considered moderately toxic, but can cause death of experimental animals at 150 ppm. It is similar to, but less toxic than, arsine and stibine and causes a hemolytic response (88,83). Germanium dioxide stimulates generation of red blood cells (83). LD_{LO} (subcutaneous) rabbit): 586 mg/kg for germanium. LD_{50} (intraperitoneal, rat): 750 mg/kg for germanium dioxide. Germanium is taken up by cereals, especially oats, from Germanium bearing soils (104).
Iron (Fe)		Because iron is homeostatically controlled, it is not toxic to man (84).	Iron is widely distributed in the environment with animal tissues usually having higher concentrations than plants. In mammals, iron is an essential element needed for the formation of hemoglobin and myoglobin. The addition of soluble iron salts in irrigation water may lead to increasing soil acidification (87).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element.	General Information	Human Health Effects	Ecological Health Effects
Lead **(Pb)**	Lead compounds usually poisonous in proportion to solubility. Toxocity of particulate lead is dependent on particle size. Lead is a cumulative poison.	Lead has many detrimental effects on humans which range greatly in severity. Acute toxicity, however, is most common in children (84). Most lead enters man in the following components of the human diet: legumes (3%), garden fruits (19%), other fruits (16%), root vegetables (6%), grain and cereal (7%), meat, fish and poultry (7%), and leafy vegetables (5%) (94.) The major routes of lead uptake in man are through the gastrointestinal tract and lungs. Of the lead ingested, 5 to 10% is absorbed and about 37% of the inhaled lead remains in the lungs. Once absorbed, lead accumulates primarily in the bones, with lesser amounts in other organs (84). Ingested lead is largely captured by the liver and excreted in bile. Lead absorbed by inhalation yeilds toxic effects from small amounts. Lead poisoning produces hemolysis of red blood cells, lesions of the kidneys, liver, male gonads, nervous system, and blood vessels. Lowest dosage, as lead, of lead compounds producing tumors in animals is 555 mg/kg. Exposure to lead increases incidence of abortions and still births. Lead is transferred across human placenta (105). Teratogenic effects in animals have been produced from exposure; lowest dosage 21 mg/kg.	Lead is present in all soils and plants. Soil contains an average of 10 to 15 μg/g and ranges from 2 to 200 μg/g of lead. The availability of lead in soils to plants is not understood. However, soil type and pH have been found to affect lead uptake. At low pH, lead is more available to plants. Plants are able to translocate lead from the soil to the roots but poorly transport it to the leaves and fruits. This occurs even when the soil lead is soluble and available in the soil (146). For example, the lead content of strawberries does not change when the lead content of soil is increased from 8 to 59 μg/g. In radishes 3 ten-fold increase in soil lead content increases the lead concentration by a factor of less than two (147). Thus is appears that soil lead may not be readily incorporated into the food chain via the soil plant pathway. There is some evidence that lead may be phytotoxic as it has been shown to decrease transpiration and photosynthesis in sunflowers (148). Roadside soils plants, earthworms, trout, and mice have been shown to have elevated lead levels which decrease rapidly with increasing distances from the highways (149,150). The toxicity of lead to freshwater organisms varies with its solubility which is a function of water hardness.

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Manganese (Mn)	Manganese compounds not highly poisonous due to manganous ion alone (155).	Manganese is an essential element for mammals , being required as a cofactor for a number of enzymes. It is present in all living organisms and is absorbed from food via the gastrointestinal tract. In general, it is not toxic to man, except from chronic inhalation of MnO_2 during occupational exposure over long periods of time (2 years) (84).	Manganese is toxic is very low concentrations to many crop plants. However, its phytotoxicity is dependent upon acidic soil conditions (87). Manganese primarily affects lower trophic levels of aquatic organisms. It has been shown to decrease growth and reproduction in some species of plankton, and cause increases in growth and reproduction in others (157).
		Strong oxidizing properties of manganates and permanganates can cause skin irritation. Exposure may cause respiratory damage.	Manganese is an essential element for mammals, being required as a cofactor for a number of enzymes. It is present in all living organisms and is absorbed from food via the gastrointestinal tract.
		Inhalation of Mn or its compounds may cause chronic poisoning (156).	Marine mollusc bioaccumulation factor of 12,000 reported (102).
		Lowest concentration causing toxic effects in humans (central nervous system effects, due to inhalation) reported to be 11 mg/m^3 (108). LD_{50} (intraperitoneal, mouse): 53 mg/kg.	Acute dose of 96-hour LC_{50} of 1,400 ppm is reported for rainbow trout (Salmo gairdneri), carp, (Cyerinus carpio), and Daphnia (145).
			Soil concentrations of 2.5 ppm have affected soybeans, but soil effects depend on variables such as pH and moisture (158).
Mercury (Hg)	May produce acute and chronic effects. Food, especially fish, is greatest contributor to the human body burden of mercury (85). Fish-eating birds and mammals, at the top of the food chain, susceptible to excessive mercury in water.	Mercury is a particularly dangerous toxicant due to its volatility and transformation by bacterial action into an akylated form (159.) It is stated that all of the organic forms of mercury (alkoxl, alkyl, and aryl) are toxic, but these mercurials in the nervous system, the ease of their transmittal across the placenta and their effect on developing tissue make them particularly dangerous to man	Mercury is a particularly dangerous toxicant due to its volatility and transformation by bacterial action into an alkylated form (159). The mercury content in soils of the United States ranges from 10 to 500 ng/g (108). Mercury tends to be retained in the surface layers of the soil due to adsorption by organic and inorganic materials and the low solubilities of mercury salts/phosphates. carbonate, sulfide) (108). Mercury has been

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Lead (contd.)			For example, brook trout are adversely affected by lead at 0.10 ng/1 in soft water, whereas in hard waters the 96-hour LC_{50} value is 442 mg/1 (87) Little is known of the biological effects of lead on marine organisms although the common marine mussel has been found to concentrate lead without showing detrimental effects (151). In addition some marine plants may concentrate each up to 40,000 times (87). Reproductive impairment of Daphnia magnia occurs at concentrations of 30µg/ℓ (102). Toxic effects in plants produced by >25 mg/ℓ in nutrient solutions (85).
Lithium (Li)	Very reactive and water soluble. Lithium is noncumulative (153).	Highly toxic to humans, partially inversely dependent on sodium intake (105). Levels above 25 µg/m³ of lithium hydride cause sneezing (133). Teratogenic dosage in rats reported to be 350 mg/kg.	Lithium is phytotoxic. The most sensitive plant species is citrus. A slight toxicity is produced by 60 to 100 µg/ℓ in irrigation water (85).
Magnesium (Mg)	Concentration of magnesium and calcium in water influences the toxicity of heavy minerals (133).	Metallic magnesium may cause local skin effects (84). Inhalation of magnesium dust can cause metal fume fever (145). LD_{LO} (oral, dog): 320 mg/kg.	At 7.2 ppm, inhibits growth of Botryococcus. 24-hour LC_{50}: equivalent to 866 ppm as Mg^{+2} for Daphnia magna (85).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Mercury (contd)		Exposure to mercury vapor results in absorption by the lungs, with some secondary amounts taken in by the skin. Absorption of elemental mercury after oral ingestion is minimal compared to the uptake of methylmercury which is quickly absorbed through the skin, lungs and gastrointestinal tract. Methylmercury tends to accumulate in the kidney, brain and blood. In addition, methylmercury may pass through the placental wall into the fetus, concentrating in the brain tissue (84). Acute illness has resulted from inhalation of 1.2 to 8.5 mg/m^3 (109). Human death has resulted from ingestion of 1,429 mg/kg (108). Central nervous system effects have resulted from inhalation of 169 µg/m^3 for 40 years(108). Certain compounds have demonstrated oncengenic potential (108,105). The lowest dosage producing tumors is 400 mg/kg. Certain compounds have demonstrated teratogenic potential. The lowest dosage producing a teratogenic response is 500 µg/kg.	reported to increase in concentration in the soils around a coal-fired power plant from 7.9 ng/g in background soils to 4.6 µg/g in enriched soils near the installation (85). In most plants, mercury concentrations range from 10 to 200 ng/g (15 ng/g average), but plants growing near mercury deposits can contain 500 to 3,500 ng/g mercury. Translocation of mercury occurs in many plant tissues, including leaves, fruit and tubers. Toxicity of mercury to terrestrial plants apparently depends more on chemical form than on its concentration. There are few studies available on the toxicity of mercury to specific plants (147). The occurrence of mercury is recognized as nearly ubiquitous in aquatic ecosystems. Most of the mercury in fish is in the methyl form (160). In addition numerous laboratory studies have demonstrated the toxicity of various mercury compounds to birds. Highest body burdens occur in fish eating birds, as compared to insect eating birds (161). Presently, little is known about the overall effects of mercury on ecosystems. However, mercury is known to cause alteration of the behavior of various aquatic organisms (162,163). Concentrations of mercury in surface waters have usually been found to be far less than 5 µg/l. Natural methylation

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Mercury (contd.)			of bottom sediment mercury in areas bordering mercury deposits results in a continuous presence of the element in solution (157). Mercury is actively taken up by lower orders of biota in freshwater quatic ecosystems. More than 75% of all the methylmercury present in these lower orders is taken up directly from the water. Higher orders of aquatic biota, such as predatory fish, take up as much as 60% of their methylmercury directly from the water. At each higher trophic level, the concentration of methylmercury has been reported to increase due to binding in the muscle tissue (164). The behavior of mercury in the marine environment is not completely understood. However, organomercurials are concentrated by marine organisms to a greater extent than are inorganic mercurials (97,165). Recently, it has been shown that the presence of selenium can decrease the toxicity of methylmercury in birds and rats (166). The presence of selenium may also result in a decreased toxicity of methylmercury in fish such as tuna, which contains high levels of selenium (167). *Oncorhynchus nerka*, *O. gorbuscha*, and *salmon eggs killed* by concentrations over 3 μg/ℓ (as mercuric sulfate).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Mercury (contd.)			Acute 96-hour LD_{50} for fish 1 mg/ℓ of inorganic mercury (85). Lesions on roses at 10 μg/m³ (37).
Molybdenum (Mo)	Molybdenum compounds exhibit a low order of toxicity for exposed workers. Molybdenum trioxide and ammonium molybdate are more toxic than the metal or the dioxide (88).	Molybdenum accumulates in the kidneys and adrenals in humans. Excretion of molybdenum in man is rapid, occurring primarily in the urine. Excess molybdenum may be excreted in the bile. No data are available documenting molybdenum toxocity in man due to industrial exposure(84).	Molybdenum is needed by bacteria, higher plants, and animals for a number of biological processes. The accumulation of molybdenum by plants is proportional to the amount added to the soil. It is not toxic to plants at natural background levels(87).
		Signs of molybdenum poisoning are loss of appetite, listlessness,diarrhea, and reduced growth rate (104).	It is concentrated by many freshwater and marine organisms including benthic algae, phytoplankton, zooplankton, molluscs, crustaceans, insect larvae and fish (101,168). Molybdenum is also essential for the fixation of elemental nitrogen by bacteria and blue green algae (169). Molybdenum exists in various valence forms. In mammals, the soluble hexavalent compounds are well absorbed, from the gastrointestianl tract and transported to the liver. Ruminants are particularly sensitive to molybdenum which they may ingest while grazing (170). A molybdenum concentration of 5 to 10μg/g is considered to be toxic to cattle (166). Sheep, horses and swine are more tolerant to molybdenum. LD_{50} (intraperitoneal, mouse): 160 mg/kg. There is an interrelation between molybdenum and copper in the nutrition

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Molybdenum (contd.)			requirements fro sheep and cattle. Copper poisoning is associated with low molybdenum levels in forage; copper starvation is associated with high molybdenum levels (153). Molybdosis of cattle was associated with lasike clover grown in soils that had 0.01 to 0.10 mg/ℓ of molybdenum in saturation extracts. Phytotoxicity is negligible, but plants accumulate molybdenum in proportion to the amount in the soil. Aquatic toxicity: Marine molluscs are reported to have a concentration factor of 60 times the concentration in water (85). 96-hr LC_{50} for fathead minnow, Pimephales promeias, is 70 mg/ℓ (for molybdic anhydride).
Nickel (Ni)	Dietary intake from plant and animal tissues are not harmful. Nickel salts are highly toxic (104). Nickel salts reported to substantially affect the biological oxidation of sewage (85).	The chemical species of nickel geratly effects its toxicity to mammals. Nickel carbonyl, $Ni(CO)_4$, is the most toxic of all the nickel compounds to man. It causes death after exposure of 30 µg/g for 30 minutes and has been implicated as a respiratory carcinogen (84). Nickel carbonyl is formed when hot carbon monoxide is passed over nickel, both os which are waste products of coal fired power plants. Dietary nickel is excreted by man largely in the feces, whereas nickel carbonyl is excreted in the urine (80). As a particulate air pollutant , nickel has been found to have deleterious health effects in both humans and other mammals (172). Exposure may cause sensitivity to nickel and dermititis. Absorption through inhalation may be associated with nasal, sinus, and lung cancer (88).	Little is known of either the soil chemistry of biological activity of nickel (108). Nickel is very toxic to many plants especially citrus fruits. At concentrations above 0.5 ng/l it will inhibit plant growth (172). Nickel is found in many soils in a generally insoluble form, but acidification may render it soluble causing plant injury or death. It now appears that the toxicity of nickel for plants may be caused by a decrease in the oxygen exchange capacity of the roots (173). As a pure metal, nickel is not a problem in water pollution because it is not affected by, or soluble in water. Many nickel salts, however, are highly soluble in water (174). Nickel salts can kill fish at

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Nickel (contd.)		Nickel in some form is probably carcinogenic in humans (173, 122). Oncogenic response minimum dosage is 16 mg/kg, as Ni.	very low concentrations. Data for the fat head minnow show death occurring in the range of 5 to 43 mg/l, depending upon the alkalinity of the water (174). Little is known of the toxic effects of nickel in marine systems. However, nickel is toxic to phytoplankton and algae. Some marine animals have been found to contain up to 400 µg/l, and marine plants up to 3,000 µg/l nickel (87). The lethal limit of nickel has been reported as low as 0.8 mg/l for some marine fish, and 1.5 mg/l for juvenile oysters (87). Concentrations 100 µg/ℓ may adversely affect several aquatic species (102). Aquatic toxicity for stickleback, 96 hour LC_{50} : equivalent to 0.26 mg/ℓ as Ni^{+2}. Concentrations of 0.5 to 1.0 mg/ℓ Ni^{+2} are toxic to tomato, oats, and other plants in sand and solution culture (85).
Phosphorous (P)	Yellow or white phosphorous is one of the most highly toxic inorganic substances (88). Red phosphorous is relatively harmless unless white phosphorous is present as an impurity.	Chronic effects in humans include liver injury, necrosis of jaw bone, anemia, brittle bones, and tooth and eye damage (83). Lowest lethal dose, administered orally, for a human is 1.4 mg/kg (108). Phosphorous may be absorbed through the skin, as well as by ingestion or through the respiratory tract (91). LD_{50} (skin, rat): 100 mg/kg.	Elemental phosphorous is highly toxic and bioaccumulates in aquatic organisms. A concentration factor as high as 25,000 has been reported with the largest concentration found in liver. LC_{50} (48 hour): 0.0105 ppm for Lepomis macrochirus (85).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Potassium (K)	The toxicity of potassium compounds is almost always that of the anion (83).	Exposure to dust or mist of potassium causes eye and respiratory trace irritation and nasal septum lesions(87).	LD_{LO} (oral, rat) potassium chloride - 2,430 mg/kg. Aquatic toxicity; 432 ppm KCl is threshold of immobilization for Daphnia magna (85). This is equivalent to 230 ppm, as K^+.
Scandium (SC)	Toxic properties are not established (83).	The oral toxicity of all the rare earth is low in man due to poor gastrointestinal absorption (84).	There is no published information on ecological effects of scandium. LD_{50} (oral, mouse): 4,000 mg/kg for scandadium chloride, $ScCl_3$. This is equivalent to 1,184 mg/kg as Sc.
Selenium (Se)		The human intake of selenium in food in seleniferous areas may range from 600 to 6,340 μg/day, which is stated to be close to the estimated levels at which symptoms of chronic selenium toxicity occur in man (87,84). Chronic symptoms in man include gastrointestinal distress, loss of hair and nails, and decayed teeth. Also reported are fetal and teratogenic effects, and fatty necrosis of the liver(84). The toxicity of selenium to man depends upon its chemical species. Elemental selenium is probably not absorbed by the gastrointestinal tract. The highest concentration in man is found in the kidneys and hair, and mainly eliminated via the urine (84). Most selenium enters the human diet through the ingestion of meat, fish and poultry (38%), and grain and cereal (62%) (94,175).	Selenium varies greatly in its soil concentration in the United States. Some areas of very high selenium content in the western U.S. have been purchased by the U.S. Government and removed from crop production. Other areas, such as the Northeast are deficient in selenium for good animal growth (23). It would thus appear that additional selenium input such as from the combustion of fossil fuels, might prove to be beneficial in certain parts of the country and deleterious in others (138,23). The soil chemistry of selenium is not understood, so that predictions of selenium uptake by plants from its soil concentration cannot reliably be made (138). In addition, selenium has not been shown to be essential for plant growth although it is concentrated by many plants to levels which are toxic to livestock (176).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Selenium (contd.)		Inhalation, ingestion or absorption through skin can cause acute and chronic effects (91). Symptoms appear similar to arsenic poisoning (102). Can cause respiratory tract irritation and systemic effects. LD_{50} (intravenous, rat): 6 mg/kg; LC_{LO} (inhalation, rat): 33 mg/kg/8 hours. No oncogenic effects from exposure reported. Teratogenic response in chicks and mice, minimum dosage 0.5 mg/kg (105).	For example, selenium at concentrations exceeding 200 μg/g (dry weight) has been found in sweet clover growing on beds of fly ash (1-7). It is stated that a concentration of selenium between 0.04 and 2 μg/g is required to prevent deficiencies in cattle, whereas concentrations of 4 to 5 μg/g are toxic (176). The deficiency of selenium in mammals results in a degenerative muscle disease. Thus, selenium is essential to mammals, but within a very narrow range and may be so for man as well. Information on the levels of selenium in freshwater and marine invertebrates and fish are limited; although it is known to concentrate in some seaweeds (87), zooplankton (178), invertebrates (179), and fish (180). It is believed that high selenium in fishes may result from high selenium content in the plankton upon which they feed (181). In addition, the selenium concentration of some aquatic organisms has been correlated with those of mercury, arsenic, and thallium (182). All of these substances inhibit pulmonary selenium excretion. This has suggested a possible regulating process in the accumulation of these elements by marine organisms (182). Several cases of livestock poisoning by selenium in waters have not been reported, although some spring and irrigation waters

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Selenium (contd.)			have been found to contain over 1 mg per liter of selenium (87). Very little is known of the potential toxicity of selenium to humans when ingested from water (87). Dangerous to aquatic environment; passes through food chain and accumulates in fish. 2.0 mg/ℓ of sodium selenite toxic to goldfish (Carassium auratus) (102). Concentrations of 0.2 kg/ha in soil can produce 1.0 to 10.5 mg/kg in tissues of forage and vegetable crops. Cattle are adversely affected by Se concentrations >4 mg/kg forage. Crop plants damaged by large accumulations. Some grain crops exhibit chlorosis. Plants exposed to Se usually show inhibition of growth (14).
Silver (Ag)	Silver is cumulative in the body.	Silver does not occur normally in animal or human tissues. The major effect of excessive exposure to silver is a local or generalized impregnation of the tissues known as argyria. It is not known to harm individuals in any way other than its unsightly appearance. Silver can be absorbed from the lungs and gastrointestinal tract. Excretion of ingested silver is primarily via the gastrointestinal tract (84).	Silver is toxic to marine organisms. It has been found to be concentrated from seawater by factors ranging from 80 for marine algae up to 1,000 for marine mammals. Concentrations of silver as low as 2μg/l have been found to delay development and cause deformations in sea urchins (87). Silver may also cause significant respiratory depression in marine teleosts after exposures to concentrations as low as 0.12 μg/g (183).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Silver (cond.)		Exposure to minor amounts over long periods produces permanent skin discoloration. Many silver salts are irritating to skin and mucous membranes (145). Skin effects noted in human exposed to 1 mg/m^3 (108). LD_{50} (oral, mouse): 100 mg/kg for colloidal silver. Intravenous administration of 700 μg/kg as colloidal silver has resulted in human death (108). LD_{50} (oral, mouse): 50 mg/kg for $AgNO_3$ (32 mg/kg, as Ag). Oncogenic effects produced by 2,400 mg/kg silver in rats.	Very toxic to aquatic species. Stickleback fish showed toxic effects at 0.005 ppm as Ag (87). LD_{50} for eggs of the American oyster, *Crassostrea virginica*, 0.006 mg/ℓ. Concentrations of silver nitrate of 1 μg/ℓ are harmful to various aquatic species (85).
Sodium (Na)	Toxic properties and health effects relate to sodium as an alkali cyanide, Na CN. Among the most rapidly acting of all poisons. Chronic poisoning is rare or nonexistent (184).	Sodium cyanide is acutely toxic by inhalation, skin absorption, and ingestion. Cyanide toxicity is an inhibition of oxygen metabolism. Human ingestion of up to nearly 5 mg/day over a long period did not result in harmful effects (102). Ingestion of 2,857 μg/kg as sodium cyanide has resulted in human death. LD_{50} (oral, rat): 6,440 μg/kg for NaCN.	Free cyanide concentrations from 0.05 to 0.01 mg/ℓ as CN have proved fatal to many sensitive fishes (85).
Strontium (Sr)	The naturally occurring isotopes are not highly toxic (154).	The biological action and function of strontium resemble those of calcium. Strontium may be essential for the growth of mammals, especially for the calcification of bones and teeth (84). No adverse effects from the industrial use of strontium have been reported. Strontium is absorbed from the gastrointestinal tract and is excreted in the urine and feces. Excess strontium is stored in the teeth and bones (84).	Strontium has not been identified as an essential trace element in either plant or animal metabolism. LD_{LO} (intravenous, rat) for $SrCl_2$: 123 Mg/kg; molecular wt $SrCl_2$: 158.5. LD_{LO} (as Sr): 87.6/158.5 x 123 = 68 mg/kg.

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Titanium (Ti)		Titanium is classified as physiologically inert to humans. Titanium is not reported as an intoxicating agent; titanium oxide dusts are considered nuisances. However, titanium tetrachloride is irritating and corrosive (83). Approximately 3% of an oral dose of titanium is absorbed by man, and of that, most is excreted via the urine. The metal, salts and oxides of titanium are all non-toxic to man, and most cases, are considered physiologically inert (84).	LC_{LO} (inhalation, mouse): 10 mg/m^3 for $TiCl_4$; molecular wt: 189.7. Aquatic toxicity: Titanium is mildly toxic to fish: 96-hr LC_{50} for fathead minnow is 8.2 ppm in soft water for titanium sulfate (85). TLm 96 (for titanium tetrachloride): 1,000 to 100 ppm (108). Titanium is effectively excluded by plants (85). There is no published record of the ecological effects of titanium.
Uranium (U)	Natural uranium is highly toxic by virtue of its biochemical activity as well as its radioactivity. The most important route of exposure to uranium is inhalation of insoluble particulate. Radiation exposure is considered cumulative.	There is no evidence linking exposure to levels of 0.15 to 0.25 mg/m^3 (both soluble and insoluble U compounds) with injury to kidney or to blood (88).	There are no data on the concentration of uranium compounds by fresh water and marine organisms. In addition, the data that are available suggest that uranyl salts are somewhat less toxic to marine than to freshwater organisms (87). Inhalation or uranium dioxide dust at a concentration of 5 mg/m^3 for five years produces no evidence of toxicity in mammals. However, uptake of the soluble uranyl ion may result in acute renal damage (84). LD_{50} (intravenous, rat): 400 mg/kg for uranium chloride, (250 mg/kg as U^{+4}). The biological half life of uranium in bone and kidney is reported as 300 days (104). Aquatic toxicity: 96-hour LC_{50} for fathead minnow, Pimephales promelas: 2.8 mg/ℓ (85).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Vanadium (V)	Vanadium is toxic by all routes of administration, with the pentavalent compounds exhibiting the highest degree of toxicity.	Vanadium has a very low order of oral toxicity to mammals. It does not affect growth, life span, nor does it produce tumors in rats or mice when given in concentrations of 5 mg/l in their dietary water (116). In humans. vanadium is excreted primarily by the kidneys. The toxic action of vanadium is largely confined to the respiratory tract. At very high concentrations (industrial exposure), gastrointestinal disorders, kidney damage, and cardiac palpitations have been observed. Heart disease has also been postulated to be related to the vanadium concentration in the air (84). Inhalation causes respiratory system effects, including tracheitis, bronchitis, pulmonary edema, and bronchial pneumonia. Dermatitis and conjunctivitis may also occur. Workers exposed to 0.5 to 2.2 mg/m^3 of V_2O_5 had eye and bronchial irritation; 0x2 to 0.5 mg/m^{3}has caused respiratory symptoms (88). Eye effects are reported at 100 µg/m^3 (108). Chronic effects have not been reported (83).	Vanadium is ubiquitous in the environment. There is some evidence that vanadium is useful and possibly essential in both mammalian and some plant systems (84,91). Vanadium is usually found in low concentrations in most soil materials, although it ranges from 20 to 500 µg/g (108). enters the atmosphere through the combustion of petroleum derivatives and coal, and then settles out on the earth's surface including the oceans (87). The ash of some oils, in fact, has been stated to contain more than 70% vanadium oxide (185). Thus, vanadium can serve as a useful indicator of the presence of other pollutants in the environment which are associated with the combustion of fossil fuels. Vanadium has been shown to accumulate in forest litter, humus, lichens, mosses and the needles of spruce trees (186). However, when present in plant culture solutions at concentrations of 0.5 µg/g or greater, vanadium is toxic to some plants (184). The accumulated vanadium, in general, remains in the roots of plants with very little reaching the stem and leaves. It is stated that plant shoots seldom contain more than 1 µg/g of vanadium (138).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Vanadium (contd.)			Information on the occurrence of vanadium in freshwater biota is lacking. There are also no reports in the literature on the toxicity of vanadium to marine organisms. However, several species of marine algae (188), invertebrate ascidians (189) and tunicates (190) concentrate vanadium to very high levels. Vanadium has a very low order of oral toxicity to mammals. It does not affect growth, life span, nor does it produce tumors in rats or mice when given in concentrations of 5 mg/l in their dietary water (116). LD$_{50}$ (oral, mouse): 23 mg/kg for vanadium pentoxide. In air, 0.5 to 1.0 $\mu g/m^3$ produced noticeable effects to plants (191). Flax, soybeans, and peas showed toxicity to vanadium at 0.5 to 2.5 mg/ℓ in nutrient solutions (85). Aquatic toxicity: 96-hour LC$_{50}$: 4.8 ppm for fathead minnow, Pimephales promelas (as vanadyl sulfate) or 1.5 ppm, as V (85).
Zinc (Zn)		In humans, zinc is concentrated the muscle, liver, kidney, and pancreas and is eliminated by the gastrointestinal tract. Zinc has been shown to be antagonistic to the detrimental effects of cadmium. Exposure to high concentrations of zinc oxide fumes results in fever in man, but this usually disappears within 24 to 48 hours (84). general, zinc is a required nutrient by man and can be considered essentially	Zinc has been shown to be essential for the growth and normal development of microorganisms, plants and animals, and is thus accumulated by most organisms. Zinc is generally uniformly distributed throughout the soil profile (108). Zinc deficiency occurs in soils in most of the agricultural areas of the United States (192). Plants vary greatly in their ability to assimilate zinc from the soil.

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Zinc (contd.)		harmless except when administered in very high dosages. Most zinc enters the human diet through the ingestion of meat, fish and poultry (37%), dairy products (21%), grain and cereal (19%), and potatoes (7%) (94). Inhalation of fumes can cause metal fume fever, with fever, nausea, vomiting, aching, cough, and weakness (145). LD_{50} (intraperitoneal, mouse): 15 mg/kg.	Tissues of plants deficient in zinc usually contain less than 15 to 20 μg/g zinc while plant tissues containing an excess of 400 μg/g zinc show toxicity symptoms (108,193). Lichens, in particular, are very sensitive to zinc and may serve as indicators of excessive zinc in the environment (194). According to the Environmental Protection Agency, in zinc mining areas, zinc has been found in waters in concentrations as high as 50 mg/l, and in effluents from metal plating works and small arms ammunition plants it may occur in significant concentrations. In most surface and ground waters, it is present only in trace amounts. There is some evidence that zinc ions are adsorbed strongly and permanently on silt, resulting in the inactivation of the metal (195.) Concentrations of zinc in excess of 5 mg/l in raw water used fro drinking water produces an undersirable taste which persists through conventional treatment (195). The acute toxicity of zinc to freshwater organisms varies greatly with the water hardness, dissolved oxygen concentration, pH, and temperature. Resistance to zinc toxicity varies between species, and may be different for juvenile and adult forms (196).

TABLE 6-7. SUMMARY OF ECOLOGICAL AND HEALTH EFFECTS

Element	General Information	Human Health Effects	Ecological Health Effects
Zinc (contd.)			For example, zinc was found to be most toxic to freshwater minnows at a pH of 8 and hardness of 50 μg/g and least toxic at pH of 6 and hardness of 200 μg/g (197). The presence of copper in water may also increase the toxicity of zinc to aquatic organisms (195). It is stated that the main concern of zinc compounds in marine waters is not one of acute toxicity, but rather the long-term sublethal effects of the metallic compounds and complexes (87). Invertebrate marine organisms are reported to be more sensitive than vertebrates to acute zinc toxicity (87). Most marine organisms often concentrate zinc to levels greatly above that present in seawater (198). While an increase in zinc intake in rats results in an increase in the concentration of zinc in their tissues, its accumulation is not great and levels fall rapidly soon after the termination of the experiment. In hard water (200 mg/ as CaCO), 0.18 mg/ of Zn reduced fertility of fathead minnow, Pimephales promelas. Rainbow trout eggs did not hatch in soft water with a concentration of 0.04 mg/ℓ of Zn. 96-hour LC_{50} for fathead minnow: 0.87 mg/ℓ Zn in soft water (20 mg/ℓ as $CaCO_3$). Concentrations of 0.4-1.6 mg/ℓ in nutrient solutions are toxic to certain varieties of soybeans (85).

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SECTION 7

RADIOLOGICAL EMISSIONS FROM SCCP'S

The burning of conventional fuels can create several pollution problems. The radiation hazard, however, is not commonly considered to be one of them, and there are fewer papers in this area. Recently, because of continued public interest in the environmental impact of nuclear power, comparisons have been made between the radiological emissions from a nuclear plant and a conventional coal power plant. The consensus of papers on this issue reports that a conventional coal-fired facility is the greater radiological polluter, (see Section 7.4). In fact, the radiological output of a lignite-fired power plant exceeds allowable limits established for a comparable nuclear facility (e.g., pressurized water or high temperature gas reactor). The long-term radiological impact of such a power plant is unknown.

The addition to their pollution considerations, radioactive trace metals have been involved with SCCP's in several other ways. Certain radioactive isotopes have been used to follow specific elements through the fuel combustion and gas cleaning and waste disposal processes. Neutron sources have been used for instrumental neutron activation analysis (INAA) for trace elements with detection in the gamma ray region. This is one of the more reliable methods to measure trace element concentrations since no sample preparation is required; see Section 8.3.5 for a complete discussion of this technique. Also, different radioactive detection methods have been used and compared. Finally, several papers address the specific environmental and health effects of incinerated radiological wastes. Almost no information was found on radioactivity associated with oil or gas combustion.

7.1 CONCENTRATIONS IN FUELS

United States coals contain three principle radioactive species: ^{238}U, ^{235}U and ^{232}Th, and their radioactive daughter products in (i.e., in the normal relative radioactive decay ratios) secular equilibrium. A summary of a U.S. Geological Survey report (1) was made in a series of similar articles of McBride et al. (2-4) and is reproduced in Table 7-1.

TABLE 7-1. RANGE OF URANIUM AND THORIUM CONCENTRATIONS AND GEOMETRIC MEANS (EXPECTED VALUES) FOR COAL SAMPLES FROM VARIOUS REGIONS OF THE UNITED STATES* (N IS THE NUMBER OF SAMPLES).

			Uranium (ppm)		Thorium (ppm)	
Region	Coal Rank	N	Range	Geometric mean	Range	Geometric mean
Pennsylvania	Anthracite	53	0.3-25.2	1.2	2.8-14.4	4.7
Applachia	Bituminous	331	<0.2-10.5	1.0	2.2-47.8	2.8
Interior	Bituminous	143	0.2-43	1.4	< 3-79	1.6
Northern Great Plains	Subbituminous, lignite	93	<0.2-2.9	0.7	<2.0-8.0	2.4
Gulf	Lignite	34	0.5-16.7	2.4	<3.0-28.4	3.0
Rocky Mountain	Bituminous, subbituminous	134	<0.2-23.8	0.8	<3.0-34.8	2.0
Alaska	Subbituminous	18	0.4-5.2	1.0	<3.0-18	3.1

SOURCE: (1)

They took 1 ppm of uranium and 2 ppm of thorium to be representative of U.S. coals. Coles et al. (5) report similar levels of U and Th from 15 western (low-sulfur) coals; they also considered ^{40}K to be significant. They report the picoCurie/g (pCi/g) concentrations, Table 72.

TABLE 7-2. RADIONUCLIDE CONCENTRATIONS IN WESTERN COALS

	ELEMENT									
	ppm			pCi/g						
Coal	U	Th	K	^{40}K	^{228}Th	^{228}Ra	^{210}Pb	^{226}Ra	^{238}U	^{235}U
Western low sulfur low ash (12 samples)	0.71	1.6	860	0.73	0.17	0.17	0.26	0.21	0.24	0.012
Western low sulfur high ash (3 samples)	2.6	5.0	1660	1.4	0.56	0.55	0.68	0.64	0.85	0.037

SOURCE: (5)

All values are valid to within at least ±20%

Cooper and Dakik (6) report that the levels of U, Ra, Th, and other radioactive isotopes in lignite appear to be significantly greater than for Western coals. The concentrations of these elements is a function of the geologic areas in which the coals are found, particularly their proximity to uranium deposits. They report that the Conquista uranium mill in South Texas roasts lignite to recover uranium. This lignite is believed to run nearly 300 ppm. Moore (7) reports that a plant in North Dakota burns lignite for the primary reason of extracing uranium from the ash residues.

Some work, focusing on other issues, has incidentally reported the concentration of radioactive elements. Tables 7-1 and 7-2 are representative of the data reported elsewhere. Many elemental determination reports give the concentrations of U and Th, but are not concerned with the level of radioactivity present in the coal. Several other papers that do include some discussion of the radiological aspects of coal are Lave (8), Martin (9), Bedrosian (10), Goldman (11), and Van Hook (12). Styron (13, 14) has also reported a radiation level from ^{210}Pb, a ^{238}U decay member, at 0.79 pCi/g for a certain western coal; he also discusses ^{210}Po. Finally, Krieger and Fishkorn at EPA (environmental Monitoring and Support Laboratory in Cincinnati) are studying the concentration of ^{226}Ra in coal and coal ash to determine the radiation hazard potential of coal burning.

No articles were found that discussed radioactive species in oil, gas, wood, or municipal wastes.

7.2 EMISSION LEVELS

More attention and effort have been directed at measuring the levels of emissions of radiological species than at source concentrations. Principally studies have looked at coal fly ash and bottom ash.

Coles et al. (5) report a 5- to 10-fold increase in the radio nuclide concentration in the fly ash over those given in Table 7-2 for the source coal. They also reported concentrations by size, showing that ^{235}U, ^{238}U, ^{226}Ra, ^{228}Ra, ^{210}Pb, show increases in radiation levels with decreasing particle size. Yet the most potent emitter was ^{40}K, ranging between 6 and 8 pCi/g, with ^{228}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb, and ^{238}U all emitting between 0.58 and 3.6 pCi/g.

McBride et al. (3) modeled a 1000 MW coal-fired power plant burning coal with 1 ppm U and 2 ppm Th. Their results are given in Curies per year for airborne emission of each major decay chain: ^{238}U chain, 8×10^{-3} Ci/yr; ^{235}U chain, 3.5×10^{-4} Ci/yr; ^{232}Th chain, 5×10^{-3} Ci/yr. They also report that radon, a short-lived decay products of Th, and U, accounts for the majority of the airborne radiation released: ^{220}Rn (1/2 life = 55 sec), 0.4 Ci/yr; ^{222}Rn (1/2 life = 3.8 days), 0.8 Ci/yr. Lyon (15), in a similar study, has developed data in agreement with McBride for U and Th and, in general, supports McBride's data.

Cooper and Dakik (6) have compiled a table of radiation release rates for the atmosphere from electrical power plants, including release rates from nuclear plants; see Table 7-3. They show that radon (the noble gas component) is the major, albeit short-lived, source of radiation emitted. Also, the radon may escape during mining and grinding, so the exact point of release is not always the same. The boiling water reactor in Table 7-3 is an old type reactor and is no longer being built. They also present scenarios for radiation release in Texas based on various energy-mixes.

Lave and Freebrug (8) consider the most significant airborne element from coal combustion to be radium; for example, ^{226}Ra, 17.2×10^{-3} Ci/yr and ^{228}Ra 10.8×10^{-3} Ci/yr for a 1000 MW plant. They also report values for a 1000 MW oil burning plant: ^{226}Ra, 0.15×10^{-3} Ci/yr and ^{228}Ra, 0.35×10^{-3} Ci/yr. The Code of Federal Regulations (16) set the allowable standard for ambient air at: ^{226}Ra, 2 pCi/m^3 and ^{228}Ra 1 pCi/m^3. In the worst case for coal, this would necessitate only a ten-fold dilution of emissions; oil plant emissions are below ambient levels.

Other articles have addressed various specific aspects of the coal-generated radiological emissions problem. Martin et al. (9) have compared radioactivity released from coal- and oil-fired steam plants (data gathered by the Bureau of Radiological Health). Bedrosian et al. (10) and Styron and Robinson (14) also have investigated some radioactive

TABLE 7-3 RADIOACTIVE ISOTOPE RELEASES TO THE ATMOSPHERE FROM ELECTRIC POWER PLANTS

	Radiation Release Rate-Curies/1,000 Mw(e)-Year			
	Noble Gas Components		Halogens and Particulates	
Type of Plant	Average	Range	Average	Range
Nuclear Plant				
Boiling Water Reactor	2,600,000.0	180,000-9,300,000	7.200	0.33-21.20
Pressurized Water Reactor	12,000.0	40-60,000	1.300	0.00007-9.10
High Temp. Gas Reactor	312.0	200-324	0.0018	0.0015-0.0020
Lignite Plant	69.0	0-475	2.000	0.050-326.00
Coal Plant	2.2	0-82	0.148	0.037-3314
Oil Plant	0.2	0-1	0.005	0.003-0.010
Gas Plant	116.0	1-232	0	0

SOURCE: 6

materials emitted from coal-fired plants. Furr et al. (14) have reported the radioactivity levels in certain fly ashes while studying the uptake of trace metals by plants grown on fly ash-soil mixtures. Of course, many studies report elemental concentrations of U and Th without reference to their radioactivity. Such data were reported in Sections 3 and 5 of this report.

Finally, several studies have looked at emissions from incinerators that burn radiologically contaminated wastes. Forster (17) summarizes practices used at three plutonium-contaminated-waste facilities. He also reports that a survey of manufacturers revealed that no commercial incinerator is designed specifically for this use. Lachapelle (18) has reported work on a 50 lb/hr incinerator and associated gas-cleaning equipment as a means to concentrate low-level radioactive wastes. Optimum conditions have been achieved and atmospheric discharges were always below emission limits. Radiologically contaminated animals were also test incinerated. Finally, Krieger and Frishkorn at EPA in Cincinnati have developed and tested a methodology to quantify discharges from nuclear medicine facilities. This included radio-pharmaceuticals not removed by tertiary sewage treatment that subsequently wind up in power plant coolant waters. However, their work has not yet been published.

7.3 HEALTH AND ENVIRONMENTAL EFFECTS

The majority of articles concerning radiation and combustion ultimately address the ecological or health impact of the process under study. McBride et al. (3) most recently have combined empirical data and modeling to assess the impact on human health from a hypothetical 1000 MW midwestern coal-fired power plant. Radium turns out to be the major source of whole-body radiation, with ingestion being the main exposure pathway; inhalation is the second major exposure pathway. Whole-body population exposures (∿20 man-rem/yr) do not exceed regulations (19) except for bone dose (∿200 man-rem/yr) nearby the plant. The U.S. average annual dose from nautral sources is 130 man-rem/year. The conclusion is that the health effects are very slight (0.002 to 0.005 health effects per year of operation per million people), and the health effects from other emissions (particulates, NO_x, SO_x) would be many times more significant.

Cooper and Dakik (6) also discuss the potential health effects of radiation from coal-fired power plants. They assumed a worst case dosage based on a hypothetical person standing 500 meters downwind from a 1000 MW power plant for an entire year. They included inhalation and ingestion of water and sediments from rainfall and settling. Different types of coals were also considered, and Table 7-4 summarizes their results. Also see Table 7-5 for regulation levels. They conclude that the whole body dosage due to national average coal-fired power plants is within (about 75%) the most stringent NRC (Nuclear Regulatory Commission) guidelines, and only the bone marrow NRC limit is exceeded; however, worst case lignite would require 99.5 to 99.8% removal efficiencies to achieve compliance.

Martin _et al_. (9) have taken fly ash data generated by the Bureau of Radiological Health on oil- and coal-fired steam stations and compared them in tabular form with limits recommended by the Inaternational Commission on Radiological Protection (ICRP). Moore _et al_. (21) have looked at sources of ^{210}Po in the atmosphere. They concluded that the major sources are dust, plant exudates and phosphate fertilizer production. They judged SCCP's to be minor contributors.

Bedrosian _et al_. (10) have made a radiological survey around fossil fuel plants (principally coal). Their primary focus was on air sampling techniques, especially those remote to the facility. But they were concerned with estimation of critical dosage to organs, particularly the lungs. Furr _et al_. (17) studied the uptake of many trace metals, including radioactive species, by cabbages grown in soil-fly ash mixtures. Goldman (11) has studied the impact of radioactivity in fly ash and concludes that it is important enough to be factored into a total assessment of coal combustion environmental impact.

Isom, Gooch and Neill (at TVA, Division of Environmental Planning, Water Quality and Ecology Branch in Sheffield, Alabama) are studying the impact of aquatic trace metals, including radiological species, released to the environment by energy generating systems (coal and nuclear). Specifically, they are looking at the bio-accumulation in the tissues and fluids of mollusks and other aquatic animals.

TABLE 7-4 MAXIMUM INDIVIDUAL RADIATION DOSE COMMITMENT LEVELS FROM TYPICAL 1,000 MEGAWATT COAL AND NUCLEAR POWER PLANTS.[a,b]

Organ	Eastern[c] Bituminous Coal	Wstern[c] Subbituminous Coal	National[c] Average Coal	South[c] Texas Lignite	Pressurized[d] Water Reactor	Boiling[d] Water Reactor	10 CFR 50 Appendix I[e] Design Guides
Whole Body	1.7	2.4	3.7	5.1	1.8	4.6	5.0
Bone	16.6	23.4	36.4	49.8	2.7	5.9	15.0
Lung	1.7	2.5	3.9	5.4	1.2	4.0	15.0
Thyroid	1.7	2.4	3.7	5.1	3.8	36.9	15.0
Kidneys	3.0	4.0	6.7	9.2	1.3	3.4	15.0
Liver	2.1	3.0	4.7	6.4	1.3	3.7	15.0
Spleen	2.6	3.5	5.4	7.4	1.1	3.7	15.0

Notes:
a. All dosage values are reported in millirems per year to a person located 500 meters downwind of the plant.
b. All dosage levels are based on calculations and data from Oak Ridge National Laboratory.(20)
c. Particulate removal efficiencies are 99.0% for all coal-fired power plants.
d. Particulate removal efficiencies are 99.99% + (DF-10,000+) for all nuclear power plants.
e. (19)

SOURCE: 6

TABLE 7-5 REGULATIONS FOR LIMITING RADIATION DOSE COMMITMENTS TO INDIVIDUAL ORGANS BY THE U.S. NUCLEAR REGULATORY COMMISSION (20).

Organ	Allowable Radiation Dose Commitment-mrem/year[d]		
	10 CFR 20[a]	40 CFR 190[b]	10 CFR 50(AI)[c]
Whole Body	500	25	5
Bone	500	25	15
Lung	1,500	25	15
Thyroid	1,500	75	15
Kidneys	1,500	25	15
Liver	1,500	25	15
Spleen	1,500	25	15
Gonads	500	25	15

Notes:
a. Currently in effect. (16)
b. To become effective December 1, 1979. (26)
c. For halogens and particulates. (19).
d. Millirems per year of radiation dose.

Morris (22) has done a modeling study to compare the risk of population exposure from a coal burning and a nuclear power plant. All of his input data are theoretical and the results predict changes in mortality in the vicinity of such plants. Braunstein et al. (23) have published several documents for ERDA on the subject of radiological impact. In one report, the environmental pathways critical to exposure are considered for ^{14}C, ^{3}H, radio-iodine, transuranics and certain other materials. They also published a bibliography entitled "Geochemical Aspects of the Behavior of Uranium and Thorium in the Environment," an in-house ORNL publication.

Styron and Robinson (14) have undertaken research on four topics; (1) to delineate the scope of potential environmental and human health problems associated with radioactivity in Western coals; (2) to establish a data base for ^{234}U, ^{238}U, ^{210}Pb, ^{210}Po, ^{230}Th and ^{226}Ra in Western coals; (3) to assess the release, fate and accumulation of radionuclides from a western coal-fired power plant; and (4) to assess the need for additional controls. They focus particularly on ^{210}Pb and found only slight increases, with dosages still below current standards.

van Hook (12) has published a summary of the current (1978) understanding of the health and environmental effects of trace elements including radionuclides from all aspects of the coal industry. Synergistic and antagonistic effects among trace contaminants are discussed. Future scenarios are considered. Finally, Cohen (24) has written an article which claims that fears of radiological hazards are overstated and the other pollutants from a coal-fired power plant are of much greater concern.

7.4 COMPARISON OF COAL AND NUCLEAR POWER

Several of the previously-cited articles ultimately compare the radiological impact of coal and nuclear power plants. The consensus of these authors is that the atmospheric emissions from a coal-fired facility are from two to ten times worse than from a nuclear power plant. There is also general agreement that the other pollutants from coal combustion are of much more concern than the radioactivity released. Specifically, these citations are (2, 9, 22, 23, 24). McBride et al. (3) specifically caution that all aspects of the coal and nuclear power generation, from mining to disposal, should be factored into any comparison of the two industries. A very comprehensive survey of the health effects of electrical generation is reported by Lave and Freeburg (8). Although they do not consider radiological emissions from SCCP's, the article directly compares health effects of coal, oil and nuclear electrical generation from beginning (mining) to end (emissions) as recommended by McBride et al.

7.5 REGULATIONS AND AMBIENT LEVELS

At the present time, there are no standards limiting radiation releases or radioactive isotope emissions from fossil fuel power plants. Nor are there any ambient air quality standards for radiation levels and radioactive isotope concentrations from fossil fuel facilities. There may be some type of standards set forth soon under the provisions of the recently promulgated Federal Clean Air Act Amendments (25).

The nuclear power industry does have standards, and fossil fuel power plant emissions are often compared to them, usually based on an equal amount of power generated. The nuclear release rates (19) are analogous to the Federal NSPS (New Source Performance Standards) administered by the EPA. Ambient radiation standards are administered by the NRC, which limit downwind exposure levels for different types of radiation (alpha, beta, gamma); these are analogous to the AAQS (Federal Ambient Air Quality Standards).

The total radiation levels in ambient air are difficult to determine since individual isotopes must be specified; however, total beta radiation, the dominant form from uranium and thorium decay processes, is often taken as representative of radiation levels in the atmosphere due to its ease of collection and measurement. Fossil fuel power plants are well below the permissible values established by the AEC. For example, the standard for total or gross beta radiation levels was set at 100 pCi/m^3; Cooper and Dakik (6) report levels in Texas range from 0.05 to 0.40 (average 0.08) pCi/m^3.

Regulations limiting radiation releases in terms of dose commitments have also been set forth by the NRC (16, 19). New standards took effect December 1, 1979 (26). These include whole body and specific organ dosages; (see Table 7-5).

The quantity of particulates released influences the total radiation release. The current NSPS of 0.10 lbs/MBtu would result in a lung dosage of 4 mrem/yr for national average coal (6), below the NRC standard (Table 7-5). However, reduction to the proposed standard of 0.05 lb/MBtu would still not achieve compliance for bone dosage.

7.6 MISCELLANEOUS TOPICS

7.6.1 Speciation and Partitioning

The major topic of the Coles et al. paper (5) is to study the chemical form and elemental partitioning of the rationuclides during coal combustion. Precipitator fly ash and bottom ash show no enrichment of ^{232}Th and its decay-chain products. Thorium and radium do show a slight size preference in fly ash. Generally, uranium shows depletion in fly ash and bottom ash and a preference for small particles. ^{226}Ra is more associated with the smaller size fly ash particles. ^{210}Pb is depleted in all ashes and shows a marked preference for small particles.

7.6.2 Atmospheric Radiation

Chamberlain (27) discusses several aspects of radioactive aerosols and vapors. While SCCP emissions are not dealt with specifically, emperical data and mathematical modeling are used to study the behavior of aerosols associated with radiological species. Aerosols from combustion products are included. Minor (28) has published a comprehensive report on many aspects of radiological air pollution. Indirectly, many topics relating to SCCP emissions are treated.

7.7 RESEARCH NEEDS

The general consensus of researchers in this field agrees that the radiation from a coal burning SCCP's, while about equal to or greater than from a comparable (in power) nuclear facility, is still not large; however, any radiation emitted into the environment is a concern, and the total amount produced by a 1000 MW coal-fired power plant is considerable. But most of the radiation is contained in the massive amount of ash and is well dispersed and believed to be of minor environmental concern.

Most researchers also agree that less than 10^{-1} Ci/yr are emitted from a typical 1000 MW plant, although there is some difference of opinion as to the major contributing species. While more research on the species emitted and their subsequent involvement in the flora and fauna of the immediate area would be useful, the radiation problem does not appear to be dire. An area of possible concern would be the bone dosage from an SCCP, particularly one burning lignite.

The long-term effects, particularly through food sources grown near the plant, may be the most urgent concern in need of more research. Also, monitoring of radiation levels in all phases of coal combustion should be continued to insure that the current levels of emission do not increase. No radiation research was found on non-fossil fuel types of SCCP emissions but, justifiably, no hazard is anticipated from these fuel sources (wood and refuse).

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SECTION 8

ACCURACY OF DATA AND ANALYTICAL TECHNIQUES

In order to understand the quality of trace metal measurements over the last 25 years, it is necessary to chronologically look at the development of sampling and analytical technology. Many research teams have contributed to the database since the 1950's using various sample preparation and analytical techniques. Care must be exercised in the comparison of the results of these efforts since different sampling, sample preparation, and analytical techniques have been used. Also, advances made in these areas have resulted in some of the more recent studies producing more accurate results.

In the middle to late 1960's, the most prevalent method for measuring trace element concentrations of coal, fly ash, and collected particulates was by atomic absorption spectroscopy. Before the sample could be analyzed, it was necessary to "prep" the sample for analysis. These preparation steps could include sample fusion or ashing, followed by liquid extraction sequences or digestion. The elemental concentrations sought by researchers could only be determined one element at a time. The element also had to be solvated in some liquid before it could be subjected to atomic absorption techniques. A commercial standard was manually prepared separately for each element, and used to calibrate the atomic absorption instrument before and after the samples were analyzed.

In the early 1970's computer technology made what appeared to be an unrelated contribution. Large core memory, high speed, second generation computers became more affordable to universities and large research centers. It was possible to write programs that allowed the millions upon millions of calculations required to translate the raw output data from X-ray diffraction (XRD), X-ray fluorescence (XRF), or instrumental neutron activation analysis (INAA) directly into trace element concentration levels in the sample. The major problem up to that time had been the accurate correction of matrix interferences of the multiple elements present in the sample. The advent of large capacity, high speed computers made such calculations possible.

The distinct advantage of INAA and XRF was that no sample preparation step was required before analysis, and all elements were analyzed for simultaneously. The data obtained from these analyses often did not agree with analysis of the same sample analyzed by atomic absorption or optical emission spectroscopy. In the early 1970's programs involving round robin analyses of the same samples were conducted by several research teams to resolve the differences in analytical values (see Section 8.3 for detailed results).

As a result of these programs the following criteria were identified for evaluating the accuracy of trace metal data:

- when (historically) were the results reported,
- by what analytical technique were the trace element values determined,
- how accurate, in general, is the analytical method employed,
- what type of standards were used to compare reported values in the study, and
- what types of internal quality assurance steps were employed in the entire research program.

Only with the answers to these five questions can the accuracy of the reported data be adequately assessed.

8.1 TYPES OF TRACE ELEMENT SAMPLING

8.1.1 Trace Element Sampling in Air

Air sampling for trace elements falls into two major categories, sampling emissions from stack gases and ambient air sampling. A large number of studies have looked at stack emissions from SCCP's, for example (1-16), and see Section 5. All of these studies use a variety of analytical techniques to obtain trace element concentrations. One study (10) used Laser-raman spectroscopy to look at fly ash particles collected from coal- and oil-fired power plants.

Several studies looked at ambient air concentrations in the vicinity of SCCP's under evaluation (11,13). In addition, a number of ambient air studies are discussed in Section 2.0 of the report.

8.1.2 Trace Element Sampling of Water

Methods of sampling water for trace elements is outlined in the manual of Methods for Chemical Analysis of Water and Waste (17). The method outlined recommends atomic absorption spectroscopy of analysis. Other methods that have been used to determine trace element concentrations in water include spark source mass spectroscopy (18) and argon plasma emission sources (19).

8.1.3 Trace Element Sampling of Soil

Soil sampling for trace elements requires some definition of what is soil. If soil is considered as the upper layer of earth that may be dug or plowed and in which plants grow, then few studies exist that have dealt with this sampling. There has been a study done on plants and soils near the Mohave generating station in southern Nevada (11). The other study was a mass balance of trace elements in Walker Branch Watershed that included some soil samples (13). One reason for the lack of such studies is given in a panel discussion on the effects of trace contaminants from coal combustion systems ERDA 77-64 (20) as follows.

The transport of trace elements within the soil hinges on water movement and chemical reactions within the soil profile. The use of available techniques for predicting and monitoring movements of soil water in the vicinity of coal burning power plants depends upon accurate field determinations of horizontal gradients in the water table and hydraulic conductivity at the sites in question. Laboratory studies of soil columns, since they do not represent field conditions, are of uncertain quality, but remain the most practical method of study (20).

8.2 ANALYTICAL TECHNIQUES USED IN TRACE ELEMENT ANALYSIS

8.2.1 Atomic Absorption Spectrophotometry

Atomic absorption spectrophotometry (AAS) can be used in determining trace elements in a nonviscous solution. Conventional atomic spectroscopy can be used to determine Li, Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ag, Cd, and Pb, after dry ashing and acid dissolution (21). A graphite furnace accessory can be used for flameless AAS determination of Bi, Se, Sn, Te, Be, Pb, As, Cd, Cr, Sb, and Ge (21).

Before a solid can be quantitatively introduced into an atomic absorption spectrometer, it must be in the form of a solution, usually in water. Depending upon the type of material, strong acids, bases and oxidizing agents can be used. Acidic digestion is most common for coal, ash and aerosols. This wet chemical procedure, although reasonably well standardized, is comparatively slow and subject to error. For example, loss of volatile elements and incomplete dissolution are the more frequent sources of error.

In atomic absorption spectroscopy, the sample in solution is atomized by a flame or other energy source producing the atomic vapor of the element being analyzed. Monochromatic light which has the same wavelength as that of the element of interest is then passed through the sample vapor. The atoms present in the ground (unexcited) state of the vapor absorb radiation from the monochromatic light source in proportion to their concentration present in the sample chamber (20,22).

Types of problems encountered in using atomic absorption spectroscopy for coal and ash samples include interelement or chemical interferences, matrix effects (which stem from the large concentrations of acids and solids in solution), and molecular absorptions (which predominantly occur from species such as strontium oxide (SrO) or calcium hydroxide ($Ca[OH]_2$) that result in a positive error in the absorption measurements) (23). Flameless atomic absorption spectroscopy achieves better sensitivity for some elements than does atomic absorption spectroscopy, and they compliment one another when used in tandem. Information on the background is necessary in addition to separation and preconcentration of the sample; therefore, a standard in the same concentration range is usually run before and after the samples.

8.2.2 Optical Emission Spectroscopy

Optical emission spectroscopy (OES) involves excitation of the sample in a spark or arc to produce a fluorescent line spectra of the elements present (24). Once again, digestion of solid samples is required prior to injection. Use of preconcentration techniques and/or a standard is required to obtain sensitivity comparable to that of other techniques such as instrumental neutron activation analysis or spark source mass spectroscopy/iosotope dilution. Nowadays, direct reading photoelectric spectrophotometers for OES offer both faster analyses and somewhat greater precision than does the use of photographic plates. Ruch *et al*. (25) achieved precision of ±10% for nine elements using direct reading detection and precision from 9% to 30% for the same samples using photographic detection (26).

8.2.3 Selective Ion Electrodes

Selective ion electrode use in trace elements analysis has been rather limited. Polarography and fluoride-ion selective electrode are methods which normally require special preparation for analysis of individual elements. Polarography is not used extensively for trace element analysis in coal or fly ash, although its sensitivity for some elements (for example, cadmium) makes it useful for trace analysis after interfering ions have been separated. Trace fluoride determinations are commonly made by fluoride-ion selective potentiometry (25).

8.2.4 Spark Source Mass Spectroscopy

Spark source mass spectroscopy (SSMS) is another analytical method used in trace element analysis. In this method, the sample compounded in a silver or graphite electrode, is ionized with a high intensity spark. A determination is then made by monitoring the intensities of the ions of different mass-to-charge ratios; different radial paths are defined in a magnetic field, and therefore, come to a focus at varying points along a photographic plate positioned on the focal plane of the magnetic analyzer. Other modes of detecting individual isotopes include scanning of the ion species at a collector slit located at the principal focus or use of electric static peak switching with static integration (18).

The method of spark-source mass spectrometry has several advantages, including high sensitivity, comprehensive element coverage, and linearity. Determinations may be made for many elements at concentrations as low as 1 ppb; also semiquantitative determinations as low as 100 ppb for some elements can be performed by electrical scanning. This technique allows detection of all elements simultaneously during an electrical scan, (including interstitial gases), with minimal spectral overlap, matrix, or inter-element effects. Also, this method exhibits linear response for ionic species of any element with the ion intensity being proportional to the concentration of that element in the sample (18).

Although detection limits SSMS for most elements in coal and fly ash are in the parts-per-billion range, accuracy may be only ±50%, varying with the concentration of interferents, as well as with data interpretation. Accuracy may be improved with the use of standards or with the use of stable isotope dilution (SSMS-ID). For elements having stable isotopes, the accuracy of this method is restricted only by the percent homogeneity of photographic emulsion on which ion intensity is recorded. Without isotope dilution, the technique is considered to be only semiquantitative.

In one study by Carter et al. (27), isotope dilution by spark source mass spectrometry and by thermal emission mass spectroscopy were used to determine composition of coal, fly ash, gasoline, and fuel oil. The average imbalance for the lower volatility elements measured by isotope dilution mass spectrometry showed a precision range from -8% to +12% (28).

8.2.5 X-Ray Fluorescence

X-ray Fluorescence (XRF) involves production of characteristic fluorescence spectra by irradiation of the sample directly with X-rays. For the analysis of air pollution particulates Birks (28, 29) cites the following advantages for this method: no sample preparation is required for filter collections, elements of atomic number 11 and greater can be analyzed with fairly uniform detectability, the technique is nondestructive, and several elements can be determined at one time with available commercial equipment at fairly low cost. Although this method does not have the submicrogram sensitivities obtainable by instrumental neutron activation analysis or spark source mass spectrometry/isotope dilution, its detection limits may be improved by using preconcentration techniques or standard reference materials. Natusch et al. (31) showed that the use of X-ray fluorescence in conjunction with other analytical techniques is a useful tool for characterization of trace elements in fly ash.

8.2.6 Instrumental Neutron Activation Analysis

Instrumental neutron activation analysis (INAA) is a nondestructive method of analysis. In this method, the sample is irradiated in a nuclear reactor directly, without chemical dissolution or extraction. When bombarded with slow neutrons, many elements give rise to radioactive isotopes. When the other components of the sample do not interfere, it is possible to identify the elements present and their concentrations from measurement of intensities of different radiation peaks emitted in the gamma ray spectrum. This method offers high sensitivity and the capability for multi-element determinations (26).

The Oak Ridge National Laboratory study at the Tennessee Valley Authority's Allen Steam Plant reported results by INAA with accuracies of 5 to 10% for submicrogram quantities (14). Carden reported accuracies of 2 to 3% in trace element studies at the Chalk Point Station using this method (31), and Ondov et al. (32) have attained accuracies in the same range.

In a recent study, four laboratories measured the concentrations of 37 elements in National Bureau of Standards standard coal samples (SRM 1632) and 41 elements in the standard reference for fly ash (SRM 1633), using instrumental neutron activation analysis. Their conclusions were as follows:

> "In some cases where comparisons can be made, both the accuracy and interlaboratory dispersion of results obtained in the analysis of coal and fly ash by nuclear methods are generally superior to other methods used in the round robin study. We suspect that the major reason for this performance of the technique is the fact that virtually no pretreatment of the samples is needed. Thus, we avoid the difficulties encountered in dissolving samples that can occur with the use of other methods such as AAS: loss of volatile species, incomplete dissolution of certain fractions, loss of elements on insoluble residues or container walls, and contamination of samples by impurities in reagents or container materials. Also, because of the long ranges of projectiles and emitted X-rays, the nuclear methods are almost completely free of matrix effects" (32).

For a few elements, the sensitivity of neutron activation can be much improved by radiochemical separations to remove those elements that have interfering radioactivities. Although these separations allow more opportunity for sample contamination, and are slower, it is possible to obtain high precision and accuracy. Radiochemical separations on low-temperature coal ash samples to determine As, Se, Zn, Cd, and Ga were carried out by Ruch _et al_. (25). However, there are cases in which INAA gives a completely false measurement due to the synthesis of elements in nuclear bombardment. For example, National Bureau of Standards studies on strontium in granite represent one such case (22).

8.3 EVALUATION OF VARIOUS ANALYTICAL TECHNIQUES

It is important to realize that data from studies using different methods for analysis are not strictly comparable because of differences in performance capabilities of various analytical methods used by different researchers. To make the evaluation of results from different studies more feasible, several investigations have been made to compare the analytical performances of several methods on the same sample (24, 33-36).

In 1973, von Lehmden _et al_. (24) undertook the comparison of six analytical methods. In this study, nine laboratories were asked to determine the concentration of 28 elements in the same coal and ash samples. The analytical methods employed were neutron activation analysis, atomic absorption, optical spectrometry and X-ray fluorescence. The determinations from the different laboratories were evaluated to assess the comparability of the various methods as applied to these matrices. Table 8-1 shows the results for the coal samples, and the ash results are given in Table 8-2. Only definitive concentrations were used for these conclusions (i.e., no "less-than" values were considered). The following conclusions may be drawn from this study:

- For at least eight trace elements in coal and ash, reported concentrations varied by more than one order of magnitude. For coal, these elements included Mn, Sb, Se, F, Li, Sn, K, and Ba. For ash, these elements were As, V, Zn, Se, Li, Ag, Sn, Na and Mag.
- Reported concentrations for three elements (Se, Li, and Sn) varied by more than an order of magnitude in both coal and ash matrices.
- Agreement was within an order of magnitude in both matrices for only 9 of the 28 elements. These nine were Si, Ca, S, Sr, Fe, Cr, Ni, Be and B.
- Standard samples must be prepared and standard methods of analysis must be developed for a range of coal and ash materials.

While this study is old by today's standard, the accuracy of these analytical techniques have improved only slightly, and the results are presumably still valid.

In an effort to resolve the analytical problems, the National Bureau of Standards (NBS), in cooperation with the Environmental Protection Agency, prepared Standard Reference Material (SRM) samples for coal (SRM #1632) and ash (SRM #1633). Portions of these samples were sent to 85 laboratories for analysis. "For many of the elements measured, there were surprisingly wide variations of concentrations reported by the participating laboratories, far outside the uncertainties usually quoted for the techniques used. For this reason, it is clear that the standards are badly needed so that laboratories can check their procedures for the elements they claim to be able to measure." (32) Thus, one must still be cautious when comparing results

TABLE 8-1. COAL ANALYSIS FOR TRACE ELEMENTS-COMPARISON OF METHODS

	Laboratory Code										
	1	3	6	1	3	2	3	4	5	3	3
	Analytical Method										
Elements Analyzed	SSMS*	SSMS*	SSMS*	OES**	OES**	NAA***	NAA***	NAA***	NAA***	NAA***	AAS
	ppm (by weight)										
Hg	< 2	< 2	< 0.10	NA	NA	< 0.2	NA	< 0.02	0.03	NA	0.051+
Be	0.4	NA	0.4	< 1	< 0.1	NA	NA	NA	NA	NA	NA
Cd	6	< 1	0.7	<30	<10	NA	< 3	< 40	NA	NA	NA
As	2	2	0.25	<100	<50	< 1	1.4	1.6	NA	< 1	NA
V	10	NA	7.7	10	10	7.0	5.5	7	NA	6.0	NA
Mn	20	3	1.9	10	20	7.6	4.8	6.7	NA	5.0	NA
Ni	<10	4	6.0	<10	<20	NA	NA	< 20	NA	NA	NA
Sb	0.6	NA	0.04	<30	<10	0.14	0.2	0.4	NA	NA	NA
Cr	<30	7	12	<10	<30	3.4	5.0	4.8	NA	NA	NA
Zn	<100	5	6.6	<100	<50	NA	NA	<100	NA	NA	NA
Cu	10	9	4.5	10	10	NA	NA	< 0.4	NA	NA	NA
Pb	< 4	4	1.8	<30	<10	NA	NA	NA	NA	NA	NA
Se	<15	< 8	0.1	NA	NA	1.0	5.0	2.0	1.5	NA	NA
B	15	5	14	10	7	NA	NA	NA	NA	NA	NA
F	< 2	4	60	NA	NA	NA	NA	NA	NA	NA	NA
Li	0.3	NA	2.8	<300	10	NA	NA	NA	NA	NA	NA
Ag	< 2	NA	< 0.1	< 1	< 1	NA	NA	< 2	NA	NA	NA
Sn	3	NA	0.19	<30	<10	NA	NA	NA	NA	NA	NA
Fe	2000	2000	1800	2000	3000	2400	2700	3140	NA	8000	NA
Sr	100	50	46	<30	NA	160	NA	120	NA	80	NA
Na	600	100	660	300	500	800	870	840	NA	800	NA
K	100	50	200	150	20	NA	2200	280	NA	100	NA
Ca	10000	10000	5800	8000	10000	NA	5500	7070	NA	NA	NA
Si	6000	10000	10000	3000	20000	NA	NA	NA	NA	NA	NA
Mg	2000	700	2000	600	100	2600	NA	920	NA	1000	NA
Ba	400	30	110	500	200	NA	220	430	NA	< 2.0	NA

*Analysis on sample direct. **DC arc on sample direct. ***Instrumental NAA. +Dissolution followed by flameless Ass.

Note: NAA, neutron activation analysis; SSMS, spark source mass spectrometry; OES, optical emission spectrometry; AAS, atomic absorption spectrometry; and NA, no analysis.

SOURCE: (24)

TABLE 8-2. FLY ASH ANALYSIS FOR TRACE ELEMENTS-COMPARISON OF METHODS

Laboratory code Analytical method Elements Analyzed, ppm[a]	1 SSMS[b]	1 SSMS[b,c]	3 SSMS[b]	6 SSMS[b]	1 OES[d]	1 OES[c,d]	3 OES[d]	3 DRES[e]	9 DRES[e]	2 NAA[f]	3 NAA[f]	4 NAA[f]	8 NAA[f]	1 AAS
Hg	1	0.4	2	0.1	1	1	NA	NA	NA	1	18	0.3	NA	0.21
Be	7	1	5	7	5	4	7	NA	3	NA	NA	NA	NA	NA
Cd	3	6	2	2.3	50	100	NA	NA	NA	NA	NA	90	NA	NA
As	40	100	15	2.8	100	200	50	NA	NA	30	70	54	40	NA
V	250	300	200	290	2000	400	200	NA	180	290	247	382	250	300
Mn	300	150	300	170	500	200	500	NA	NA	317	294	369	250	NA
Ni	100	100	100	45	300	50	300	NA	NA	NA	NA	NA	NA	100
Sb	10	40	NA	5.6	50	100	NA	NA	NA	9.2	7	19	NA	NA
Cr	200	100	100	330	500	100	300	NA	80	108	100	130	NA	150
Zn	200	70	1000	330	100	200	200	NA	350	NA	NA	NA	NA	600
Cu	100	150	200	45	300	200	300	NA	NA	NA	NA	33	NA	90
Fb	200	200	100	180	100	200	200	NA	440	NA	NA	NA	NA	95
Se	10	15	NA	0.77	NA	NA	NA	NA	NA	8.2	40	12	NA	NA
B	500	200	300	190	300	300	500	NA	NA	NA	NA	NA	NA	NA
F	30	10	100 max	60	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Li	20	60	150	190	20	100	300	NA	NA	NA	NA	NA	NA	NA
Ag	1	2	NA	0.04	3	2	1	NA	NA	NA	NA	NA	NA	NA
Sn	6	15	NA	1.9	20	100	NA	NA	NA	NA	NA	NA	NA	NA
Fe	High	High	10%	5.3%	20%	10%	5.0%	10.5%	13%	17.5%	18.3%	18.1%	26%	17.8%
Sr	150	200	200	69	200	200	500	NA	400	520	NA	180	1000	NA
Na	2000	2000	500	6600	3000	4000	3000	1400	NA	2700	2300	2450	3500	2800
K	High	High	1.%	1.7%	2%	2%	0.5%	NA	NA	NA	1.5%	3.1%	2.5%	2.0%
Ca	High	High	4.0%	1.3%	5%	5%	3.0%	3.7%	3.7%	NA	2.2%	3.9%	NA	4.7%
Si	High	High	10%	major	20%	15%	20%	NA	NA	NA	NA	NA	NA	19.5%
Mg	10000	10000	5000	44000	5000	4000	5000	4000	2200	13700	7000	3000	4000	6000
Ba	200	600	700	110	200	300	500	NA	NA	NA	200	410	400	NA

a-ppm by weight, higher concentrations are specified as percent (%).
b-Analysis on sample direct.
c-Duplicate sample submitted for SSMS and OES analysis only.
d-DC arc on sample direct.
e-Dissolution followed by RF spark analysis.
f-Instrumental NAA

SOURCE: (24)

Note: Analysis Code-NAA, neutron activation analysis; SSMS, spark source mass spectrometry; OEC, optical emission spectrometry; DRES, direct reading emission spectrometry; AAS, atomic absorption spectrometry; NA, no analysis.

from different labs -- especially results before the availability of the NBS standards in 1976.

In the study by Ondov et al. (32), four participating laboratories measured the concentrations of 37 elements in the NBS standard coal sample and 41 elements in fly ash. The analyses were performed by instrumental neutron activation, photon activation and natural radioactivity. The latter method was used by one laboratory to determine K, Th, and U. Both the accuracy and interlaboratory dispersion of results for these methods are generally superior to those for the other methods discussed.

While the results of the neutron activation analysis from this study were good, there is still a need to develop standard procedures for the other methods of analysis. To this end, a task group under the D-5 committee of the American Society for Testing and Materials (ASTM) has been conducting a round-robin analysis of coal and ash. Work has been essentially completed on the development of standardized methods for the analysis for some trace elements (F, Hg, Be, Cr, Cu, Mn, Ni, Pb, V, Zn) and for the major constituents. It is expected that these methods will appear as ASTM standards in 1980.

The data on trace element concentrations from research beginning in 1977 is probably generating the most accurate data to date. Standard Reference Materials (SRM's) for coal and fly ash have been made available by the National Bureau of Standards since 1976. Most current studies make use of these standards in their analytical programs. This provides a consistant reference point to compare data from different studies. INAA and XRF analysis programs are becoming more widespread in their usage; however, the analysis cost per sample is still relatively expensive.

Several examples of ongoing work are included here to give the reader a feel for current areas of research. J.H. Steinfield, working at the California Institute of Technology graduate school, is working to develop a low-pressure impactor of fractionating particles below 0.5 micrometer diameter. He wants to use this impactor in conjunction with combustion studies and in measurements of trace metal concentrations in the vicinity of power plant plumes. C. E. Cushing, sponsored by Battelle Memorial Ecosystems in Washington is studying the effects and behavior of fossil fuel effluents in freshwater ecosystems. At the University of California Agriculture Experiment Station at Riverside, California, G. R. Bradford is doing a trace element study of soil-plant-water systems. The environmental fate of emissions from coal plants is being examined by R. R. Turner et al. at Oak Ridge, Tennessee, under the sponsorship of ERDA, Division of Biomedical and Environmental Research.

On the horizon is one of the most promising and least expensive analytical techniques, ion plasma. Ion plasma allows simultaneous determination of up to 36 elements in a sample in less than two minutes. Most matrix interferences are eliminated. Current research studies are evaluating the elimination of any sample preparation before analysis to allow direct introduction of the solid sample into the plasma. This method of analysis is most promising for fast, low cost, reliable elemental analysis.

8.4 AREAS WHERE FURTHER EVALUATION IS REQUIRED

Determination of adverse ecological or health effects of combustion-derived trace contaminants is dependent upon characterization; that is, a complete chemical and physical description of materials entering the environment from these systems is required. Anthropogenic contaminants enter the environment via two primary pathways: (1) emission into the atmosphere with the consequent potential for long-range transport and remote impact, and (2) direct discharge via runoff and leaching into the aquatic and terrestrial domain where impact might be expected to be more localized. Of primary importance to the characterization process in either case is complete and accurate analysis of selected representative samples obtained from the various effluent streams of the combustion system.

8.4.1 Evaluation of Current Status

A degree of caution is necessary in preparing a general statement of the current status of characterization and analysis of trace contaminants from SCCP's. A number of careful characterization studies have been completed (32, 37-43), and a statement stressing current limitations may tend to detract from this work. On the other hand, in virtually every aspect of the problem, there are a variety of difficulties that remain to be overcome.

8.4.2 Current Sampling Status

The problems associated with sampling atmospheric emissions from SCCP's are substantial. Currently available information indicates that the chemistry of fly ash and aerosols varies with particle size (37, 42-44), that some elements tend to concentrate on particle surfaces (45, 43, 44), and that some elements are present in the gas phase (46, 47, 43, 44). In addition, there is evidence that the combustion and stack gas temperatures strongly influence the distribution of elements between phases (46, 43).

A good deal of current interest and effort is on particle sizing. The concentration of many trace elements is known to vary with particle size (Sections 3, 4). Also, the efficiency of control devices is primarily a function of size, as is the interaction of the particulates with the environment (Sections 4, 6). But none of the accepted sizing methods are fully satisfactory. For SCCP sampling, differential impactors (e.g., Andersen cascade impactor, Brink impactor, University of Washington impactor, etc.) are nearly always used, but they are known to fall short of desired capability; a series of reports by Southern Research Institute (48-50) adequately discusses the problems. Better particle sizing data would improve understanding in several areas of SCCP emissions: particle formation mechanisms; trace metal distribution and activity; control technology; environmental transport, residence time, and interaction material. Indeed, more research into sampling techniques that provide for better sizing information would be welcomed by several disciplines.

There is also evidence that organic materials of high molecular weight and low volatility may be present in the gas phase at the temperature of the flue gas, but that they rapidly condense on available surfaces (e.g., fly ash in the stack plume) as the plume disperses and cools (42, 53). A similar phenomenon occurs with certain trace metals which vaporize and condense on fly ash particles. The partitioning of these materials, as with volatile organic materials, is a strong function of flue gas temperature. Thus, to fully characterize stack emissions, it is necessary to sample both condensed and gas phases and perhaps to sample at various distances from the mouth of the stack for both organic and inorganic phases. The development of aircraft-compatible sampling systems may well facilitate the study of power plant emissions. In any event, the sampling trains currently being developed and proposed for instack sampling are promising, but they are still in development. They are probably not adequate for quantitative collection of specific materials, but they may be adequate for the collection of sufficient material for identification of the specific trace substances that may be present in the gas and condensed phases.

As with atmospheric emissions, sampling and characterizing wastewater streams, runoff, and aquatic/terrestrial systems appears to be a difficult problem. In addition, there is often the questions as to whether the organic materials and trace metals are dissolved in water or adsorbed on suspended and sedimentary solids. Preservation of the samples prior to analysis is often a problem; freezing samples seems to be the most effective procedure at present. A better approach to overcoming the preservation problem may be to develop more sensitive analytical procedures that require only a small water sample (a few milliliters); then field sampling would be possible in which the sample is fractionated and/or concentrated when collected and then transported to the laboratory for study. The problems mentioned above relating to subsequent sample analysis still need to be faced (51).

There are at present, no well-defined and standardized sampling procedures that permit comparison of results obtained in different studies. This is especially true for aqueous, soil, and biological sampling where the difficulties associated with obtaining and preserving truly representative samples are substantial. The sampling problems associated with inorganic analysis of materials from aquatic or terrestrial environments appear, in fact, to be related mainly to the representativeness of the sample. The sampling strategy must assure that samples obtained can be used to estimate the state of the system as a whole. By way of illustration, when the size of coal piles and ash ponds associated with utility coal combustion systems is considered, the magnitude and complexity of obtaining a representative sample is obvious.

8.4.3 Evaluation of Analysis and Instrumentation

Analytical methods are available for most elemental analyses and, with few exceptions, their sensitivity and accuracy are adequate for the characterization of trace contaminants. This statement should not be interpreted as suggesting that there is not a continuing need for improved analytical techniques that can provide greater sensitivity, reduced cost, and broader applicability. For example, there are few methods available with the capability of multi-element analysis in a variety of matrices without digestion. It is believed, however, that the characterization of effluents is not prevented by any fundamental inability to perform elemental analyses, but it should be recognized that the cost, in terms of skilled and highly trained personnel and sophisticated instrumentation, may be very high.

Because the coal being burned provides the source for trace metal emissions, a knowledge of the elemental concentration in the various coals is vital. Work to date shows that there is considerable variation in trace element composition not only with coal rank but also with geographical origin (52) (see Section 3). Current techniques and instrumentation are capable of assessing the concentrations of trace elements in the various coal materials. Currently, only a few laboratories have a total trace element capability. Problems still exist in dealing with the more volatile elements at very low concentrations (53). While these determinations can be performed at levels less than 1 ppm, the time and expense are prohibitive for all but the most essential cases.

An analytical problem associated directly with coal analysis is that of low temperature ashing (54, 51); standardized procedures and behavioral characteristics for different coals have not yet been established. Because such procedures are not widely used, an exchange of information is needed to inform users of the significant variations in results that do arise as a result of the variability of different coals; see Section 3.

Over the next 10 to 20 years, ash from power plants will be one of the most significant waste disposal problems in this country. It is known that ash contains a large number of potentially toxic elements. In view of this massive quantity of solid wastes, the possibility must be considered that trace contaminants (principally heavy metals) will enter the environment, and in order to predict the environmental contamination, something should be known of the distribution of trace metals in ash. Bulk analyses are not sufficient. In addition, the chemical form in which the metals occur in ash should be known. At present, there exists a plethora of data on the bulk composition of ash, but too little is known of the distribution of elements and practically nothing is available on speciation of trace contaminants.

Speciation studies are difficult at best. With a few exceptions, there really is no direct means of identifying the species association(s) of a trace element. Most techniques serve mainly to eliminate possibilities and to indicate likely sites for an element. Electron spectroscopy for chemical analysis provides information on the oxidation state of elements on the surface but does not identify chemical species directly (55). Conclusions are drawn to a large extent on circumstantial evidence. In simple 2-, 3-, or 4-component systems, fairly precise information on speciation can be obtained. This is not true, however, for complex systems. Inasmuch as most heavy metals in ash are probably ionic, analysts are forced to study speciation in the solid state and cannot employ analytical methods utilizing solution chemistry.

In attempting to develop methods to determine the inorganic species present, the use of physical separations as a pretreatment appears to offer a partial solution. With soils and bottom sediments, considerable success has been achieved by first separating the sample into a number of size fractions, using standard methods (sieving, settling columns, centrifugation). Further segregation is obtained on the basis of specific gravity using continuous density gradient centrifugation (size segregation is essential before using density procedures) (34, 56). Such techniques are capable of separating particles with specific gravity differences as little as 0.05.

The above two-fold physical separation yields fractions that are much more homogeneous than the original sample, thereby making the interpretations of speciation data more reliable. Speciation is also a problem in characterization of atmospheric emissions. In this area, some progress has been made on real-time monitoring of particles in-situ in aerosols by light scattering (57-58). When plane-polarized light scattering is coupled with ordinary light scattering, it is possible to measure particle size distribution and to obtain compositional information. This technique has a distinct advantage in that it circumvents many of the current sampling problems while providing real-time data and size-composition relationships.

Single particle analysis is applicable to speciation studies for both atmospheric and aquatic/terrestrial samples. The state-of-the-art of single particle analysis has advanced remarkably during the past several years. Secondary ion mass spectrometry and Auger electron spectrometry have been successfully employed in identification of trace elements in airborne particles. Techniques have been developed and reference data have been obtained that permit identification of inorganic particles by morphological characterization or optical microscopy, often supplemented by scanning electron microscopy.

The capability of X-ray fluorescence spectroscopy and X-ray diffraction measurement of small particles is encouraging, but further development is needed. A recent development in single particle analysis has been the application of micro-Raman spectroscopy. Single particles in the respirable range (i.e. <10 μm) have been examined for $SO_4^{=}$ and NO_3^{-} (59). This technique is promising and, with increased sensitivity, should provide important data relevant to coal combustion systems, including trace element speciation.

8.4.4 Standard Materials and Methods

For any large undertaking requiring the analytical efforts of a number of laboratories, it is essential that sufficient attention be given to quality assurance to establish that the data are sufficiently comparable to meet the needs of the task. For the task of characterization and analysis of trace contaminants from coal combustion, very accurate data are probably unnecessary; nevertheless, there is a need for widely accepted and used (standard) methods and for suitable Standard Reference Materials (SRM). Currently available SRM's for trace elements in coal and coal-related substances may not be adequate (60).

In addition to the need for SRMs, the complexity and variability of the materials to be analyzed in characterizing trace contaminants from coal and coal combustion suggest the need for employing standard methods. This is especially true when undertaking the comparison of emissions from various combustion processes (e.g., conventional combustion compared with fluidized bed combustion, and the influence of various operating parameters and configurations on the nature of the effluents from combustion systems). Documented standard methods are currently available for only a very limited number of analyses and have been developed primarily for use in commerce (ASTM). Standard sampling methods for the purpose of trace contaminant measurement are essentially nonexistent (60, 53).

8.4.5 Characterization Studies

A greater emphasis has been placed on coal combustion because 5-20% of the initial quantity of coal combusted remains as ash. Whereas for oil, about 0.1% of the total quantity of oil combusted remains as ash (see Section 3 of this report); therefore, the quantities of waste produced are much larger in coal combustion as opposed to oil. Much less emphases has been placed by researchers on characterization of the combustion of trash or wood. These two fuel sources are just now being considered as alternate fuels for use by industry and consumers to generate useful heat from their combustion. Little emphasis has been placed on the study of gas-fired SCCP's because gas is normally such a clean-burning fuel. Also, due to rising price and Federal Regulations, the use of gas in industrial and utility boilers is being phased out.

As noted in the introductory remarks for this section, a number of field characterizations of trace element emissions have already been undertaken. For the most part, these have been of limited scope with regard to the variety of contaminants measured, the diversity of effluent streams investigated, and the range of operating parameters addressed by the study. As a result, much valuable information has been gained on specific systems, but the ability to generalize and predict is still quite limited.

By far, the greatest mass of inorganic trace contaminants leaving a coal combustion system is deposited directly on the land and into surface and ground waters through ponding of ash and the discharge of various wastewater streams. Typical process waters or wastestreams generated in coal combustion facilities that contain trace elements include: ash sluice water, coal pile drainage, ash leachates, coal leachates, SO_2 scrubber sludges and supernatant, chemical cleaning wastes, and boiler blowdown (61). See Section 4 for a more complete description of these streams, and Section 5 for quantitative results on their trace metal content.

Many of these wastestreams have undergone initial characterization (62); however, the results of the initial work in many cases is limited in its predictive applicability due to differences in fossil fuels, in plant operations, and in geographical-meteorological differences of study sites. In addition, many of the characterization studies completed or under way rely heavily on laboratory studies rather than full-scale field sampling efforts.

To fully characterize trace contaminant emissions, it is necessary to conduct further studies aimed at identifying the effects of various firing parameters, boiler designs, and emission control techniques (e.g., SO_2 scrubbers, hot-side precipitators, etc.). In this connection there is a role for basic research in combustion processes, reaction kinetics, and thermodynamics that may provide insight into the fundamental processes that determine the pathway of the various trace elements present in fossil fuels through the entire SCCP.

In addition, controlled laboratory studies of those factors that influence the availability of contaminants, such as leachability, should be carried out in support of field studies. Such information could greatly reduce the number of characterization studies needed to predict the emissions that might be expected from a particular combustion system burning a particular coal (43, 30).

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SECTION 9

REGULATIONS

It is the purpose of this chapter to present to the reader a brief history of Federal environmental acts and regulations since 1970. Only acts and regulations that have bearing upon SCCP's will be considered. After the reader is aware of the actions that have taken place to establish regulations for SCCP's in areas other than trace metal emissions, then the current regulatory climate and the possible need to take further Federal action to limit trace metal emissions can be evaluated. As the scenario is presented, the informed reader can assure himself that a definite relationship exists between point source SCCP's particulate emissions and trace metal emissions. Currently there does not exist a Federal regulation that specifically limits the emission of trace elements from SCCP's. However, in the current regulatory climate, this could be negated in the near future.

Since regulations already exist for total suspended particles in ambient air, the regulatory framework already exists if trace metal emission regulations are deemed necessary. This regulatory framework can support the enforcement of trace metal emissions through such vehicles as the issuing of permits and source compliance sampling, already in effect.

The real decision that must be made is whether information gathered thus far under current regulatory sanctions is sufficient to determine if other trace metal emissions regulations are needed. If not, then what areas of further study and evaluation are necessary to make an intelligent decision?

9.1 FEDERAL ENVIRONMENTAL REGULATORY ACTS SINCE 1970

9.1.1 Clean Air Amendments of 1970

In 1963 the Clean Air Act was promulgated. In part echoing the 1955 act, this new act provided for matching funds to state and local agencies for air quality control, research and training programs. Additionally, the act called for control of air pollution from Federal facilities, and the supervision of interstate transport of pollution. In 1965, the 1963 act was amended to include Federal emission standards for motor vehicles. The amendment became known as the Motor Vehicle Air Pollution Control Act. In 1967 Congress passed the Clean Air Act. Its major objectives were to protect the public health and welfare and the productive capacity of its population, to reduce harmful emissions, and to insure that air pollution problems will, in the future, be controlled in a systematic way (1, 2). The act also directed HEW to designate air quality control regions, develop air quality criteria documents, publish reports on control techniques, establish air quality standards and initiate the development of implementation plans.

It was not until the establishment of the Environmental Protection Agency (EPA) in 1970 that an organized effort to protect the nation's environment was undertaken. The control steps as prescribed by the amendments (3) are briefly reviewed below.

9.1.1.1 Air Quality Control Regions (Sec 107) --

A systematic control of air quality can only be conducted effectively in areal entities with common problems (2). For this reason air quality control regions were designated on the basis of meteorological data and topographic features including the types of functional areas and jurisdictional boundaries which are important in the implementation of air quality standards. EPA established the boundaries in consultation with local authorities and concerned citizens.

Once approved, the boundaries were published in the Federal Register and the air quality control regions were officially designated (4). In order to get this process off to a quick start, the Clean Air Amendments gave the EPA 90 days to complete this task (2). To date, 247 air quality control regions have been established, of which 65 are interstate and 182 are intrastate regions (5). Figure 9-1 shows the distribution of air quality control regions in the U.S. (6).

9.1.1.2 Air Quality Criteria (Sec 108) (3)--

As a next logical step, EPA was required by the amendments to develop air quality criteria for the pollutants, particulate matter, sulfur dioxide, carbon monoxide, hydrocarbons, photochemical oxidants and nitrogen oxides (7-9). These criteria were based on the latest scientific knowledge, given concentrations at which specific pollutants, either by themselves or in combination with other pollutants, produce identifiable adverse effects on the health and welfare of the public (2). Air quality criteria merely describe the effects which are likely to occur when a certain pollutant concentration is exceeded for a specific length of time. Air quality standards, on the other hand, legally prescribe the pollutant concentrations which cannot be exceeded more than once per year in a certain air quality control region for a specified standard setting time.

Additionally, the EPA was required by law to publish reports on the latest control techniques available for emission reduction of regulated pollutants (10). These reports had to not only discuss the latest technology, but also had to include the costs of control devices, and the costs and feasibility of alternative control measures. From time to time the EPA was required to revise these documents as new information became available (2).

9.1.1.3 Ambient Air Quality Standards--

Air quality criteria were defined and numerical concentration levels were established. When promulgated, these values become ambient air quality standards (AAQS's). There are national primary AAQS's which are set to protect the public health, and secondary AAQS's which are set to insure the public welfare. The national AAQS's set the upper limit and apply to all air quality control regions. But each control region has the option to set standards which are more stringent than the federal standards (11). Table 9-1 gives the list of national ambient air quality standards with sampling methods (12).

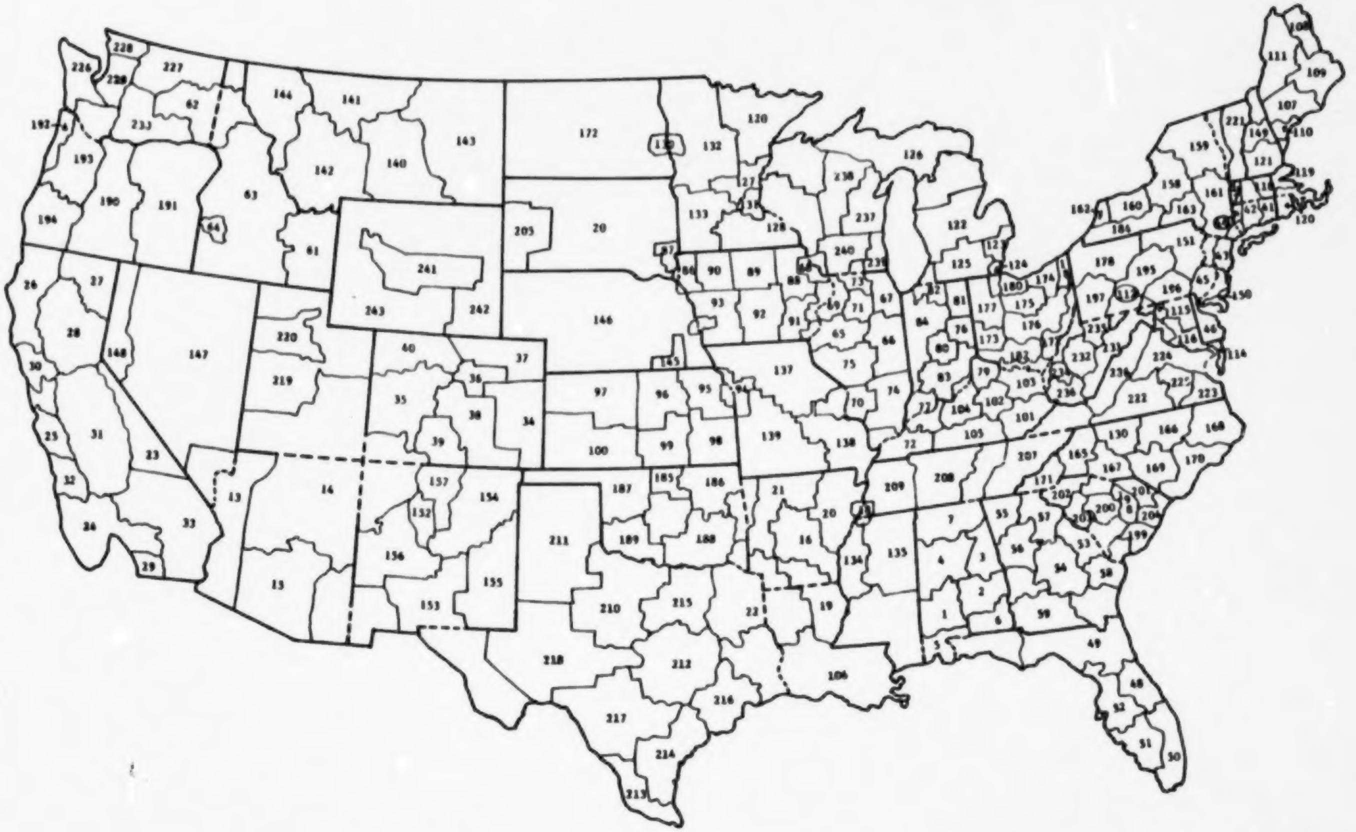

Figure 9-1. Boundaries of air quality control regions.

SOURCE: (6)

NOT SHOWN

6 Cook Inlet (Alaska)
9 Northern Alaska
11 South Eastern Alaska
60 Hawaii

TABLE 9-1. NATIONAL AMBIENT AIR QUALITY STANDARDS

Pollutant	Averaging Time	National Standards Primary	 Secondary	Sampling Method
Suspended Particulates	Annual geometric mean	75$\mu g/m^3$	60$\mu g/m^3$	high-volume
	24-hr. maximum*	260$\mu g/m^3$	150$\mu g/m^3$	
Sulfur dioxide	Annual arithmetic mean	80$\mu g/m^3$ (0.03 ppm)	60$\mu g/m^3$ (0.02 ppm)	modified pararosaniline or equivalent[1]
	24-hr. maximum*	365$\mu g/m^3$ (0.14 ppm)	260$\mu g/m^3$ (0.10 ppm)	
	3-hr. maximum*		1300$\mu g/m^3$ (0.50 ppm)	
Carbon monoxide	8-hr. maximum*	10mg/m^3 (9 ppm)		nondispersive infrared spectroscopy or equivalent[2]
	1-hr. maximum*	40mg/m^3 (35 ppm)		
Hydrocarbons (corrected for methane)	3-hr. maximum* (6-9 AM)	160$\mu g/m^3$ (0.24 ppm)		Flame ionization detection using gas chromatography
Photochemical oxidants (corrected for dioxide)	1-hr. maximum*	160$\mu g/m^3$ (0.08 ppm)		Chemiluminescence or equivalent[3]
Nitrogen dioxide	Annual arithmetic mean	100$\mu g/m^3$ (0.05 ppm)		Jacobs-Hochheiser or equivalent[4]

*Not to be exceeded more than once per year.

[1] coulometric and flame photometric methods.

[2] gas chromatography and mercury replacement.

[3] neutral potassium iodide colorimetric and coulometric methods.

[4] Saltzman and coulometric methods.

Data Source: (11).

9.1.1.4 Standards of Performance (Sec. 111)--

Under the amendments, the EPA is also required to set standards of performance, as emission standards, for all new and modified stationary pollution sources (13, 14). In contrast to AAQS's which set limits to the ambient pollutant levels, standards of performance constitute limits at the source in such a way that AAQS's for the respective pollutants should not be exceeded. Table 9-2 presents standards of performance for twelve source categories currently identified (15, 16). These are the new Source Performance Standards (NSPS). For all old and unmodified sources of the categories in Table 9-2, states must set their own performance standards using guidelines provided by the EPA.

9.1.1.5 Hazardous Air Pollutants (Sec. 112)--

Three pollutants, namely asbestos, beryllium and mercury have been singled out as being potentially more toxic at concentrations found in the atmosphere than those pollutants for which AAQS's have been set. A technical report has been published for each of the three substances. These reports address the nature of the substance, the adverse health effects, the economic impacts if standards are enforced, and the difficulty of identifying a potentially hazardous level for these substances which are highly toxic at minute concentrations (17).

9.1.1.6 Air Quality Surveillance--

In 1961 a sophisticated air sampling network, the Continuous Air Monitoring Program (CAMP) was established (19). Fully automatic instruments continuously recorded the concentrations of nitric oxide, nitrogen dioxide, sulfur dioxide, total hydrocarbons, carbon monoxide, total oxidants and ozone. The cities of Chicago, Cincinnati, New Orleans, Philadelphia, San Francisco and Washington D.C. were initially selected for this study.

TABLE 9-2. NATIONAL STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Source	Pollutant	Emission Standard
1. Fossil fuel-fired steam generators	Particulate matter	0.1 lb/10^6 Btu (maximum 2-hr average)
	Sulfur dioxide	
	coal-fired	1.2 lb/10^6 Btu (maximum 2-hr average)
	oil-fired	0.8 lb/10^6 Btu
	Nitrogen oxides	
	coal-fired	0.7 lb/10^6 Btu (maximum 2-hr average as nitrogen dioxide)
	oil-fired	0.3 lb/10^6 Btu
	gas-fired	0.2 lb/10^6 Btu
	Visible pollutants	<20% opacity, except in any 1-hr emissions may be as much as 40% opacity for 2 minutes
Incinerators	Particulate matter	0.08 gr/scf
3. Portland cement plants	Particulate matter	
	kilns	0.3 lb/t of feed
	clinker coolers	0.1 lb/t of feed
	Visible pollutants	
	kilns	10% opacity
	others	<10% opacity
4. Nitric acid plants	Nitrogen oxides	3 lb/t of acid
	Visible pollutants	<10% opacity
5. Sulfuric acid plants	Sulfur dioxide	4 lb/t of acid
	Acid mist	0.15 lb/t of acid
	Visible pollutants	<10% opacity
6. Asphalt concrete plants	Particulate matter	90 mg/dscm[a] (0.04 gr/dscf)[b]
	Gases	<20% opacity
Petroleum refineries	Particulate matter	1.0 kg/1000 kg (1.0 lb/1000 lb) of coke burn-off
	Gases	<30% opacity, except for 3 minutes in any 1 hour
	Carbon monixide	<0.05% by volume
	Sulfur dioxide	<230 mg/dscm (0.10 gr/dscf) of H_1S in and fuel gas
8. Storage vessels for petroleum liquids	Hydrocarbons	Storage vessel with vapor pressure from 78 mm Hg (1.5 psia)[c] to 570 mm Hg (11.1 psia) must have floating roof, vapor recovery system, or equivalents; for vapor pressure 570 mm Hg vapor recovery system or equivalent required
9. Secondary lead smelters	Particulate matter	50 mg/dscm (0.022 gr/dscf) from blast or reverberatory furnice
	Gases	<20% opacity
10. Secondary brass and bronze ingot production plants	Particulate matter	50 mg/dscm (0.022 gr/dscf) from reverberatory furnice
	Gases	<20% opacity
11. Iron and steel plants	Particulate matter	50 mg/dscm (0.022 gr/dscf)
12. Sewage treatment plants	Particulate matter	0.65 g/kg dry sludge input (1.3 lb/t)
	Gases	<20% opacity

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[a] dscm - dry cubic meter at standard conditions [20°C (68°F), 760 mm Hg (29.92 in. Hg)]

[b] dscf - dry cubic feet at standard conditions

[c] psia - pounds per square inch absolute

Data Source: (15, 16, 18)

Since 1968, most of the nation's air pollution monitoring has been carried out by three National Air Surveillance Networks: the high-volume network, the gas sampling network, and the CAMP station network. Since 1970, these three networks have been part of the National Air surveillance Network (NASN) operated under the auspices of the EPA. In 1971, the NASN program consisted of some 7,000 air pollutant samplers, of which some 3,500 were of the static type (e.g., deposit gauges); some 2,400 were mechanical devices of the integrating type (e.g., high-volume samplers); some 460 were spot tape samplers and some 235 were various types of automatic and continuous sampler/analyzers (20).

Monitoring and data analysis are carried out within the Office of Air and Water Programs, which, with its Air Pollution Technical Information Center, is a subdivision of the EPA. Processing and analysis of the huge amounts of data is handled by an automated system for the Storage and Retrieval of Aerometric Data (SAROAD) (2). The collection and dissemination of aerometric data to and from the National Aerometric Data Bank (NADB) is handled through the National Aerometric Data Information Service (NADIS). The data is transmitted from local to state agency, and then to NADB, by data phone, magnetic tape, punched cards, or paper forms.

9.1.2 Resource Conservation and Recovery Act of 1976 (RCRA)

The 1976 amendments to the Solid Waste Disposal Act, titled the Resource Conservation and Recovery Act of 1976 (RCRA), mandate national action for the first time against solid waste management practices that lead to environmental and public health hazards (21, 22). They also seek to promote resource recovery and conservation as waste management options. The main provisions of RCRA for achieving these goals are as follows:

- Federal financial and technical assistance to State and local governments is authorized for planning and development of comprehensive solid waste management programs that include environmental controls on all land disposal of solid wastes, regulation of hazardous wastes from point of generation through disposal, and resource recovery and conservation activities.

- Such programs would include schedules for upgrading or closing all environmentally unacceptable land disposal sites ("open dumps") identified according to EPA criteria and a nationwide inventory. Open dumping is prohibited except as covered by an acceptable schedule for compliance under the State plan.

- Where states do not establish hazardous waste regulatory programs that meet Federal standards, EPA will administer regulatory control.

- A Cabinet-level interagency study of resource conservation policies is mandated; findings and recommendations are to be submitted periodically to the President and the Congress.

- Public participation is required in the development of all regulations, guidelines, and programs under the Act.

- Research, demonstrations, studies, and information activities related to a wide range of solid waste problems are authorized.

SOURCE: (21)

The Resource Conservation and Recovery Act of 1976 creates Federal and State regulatory authority over both solid and hazardous wastes. Key definitions in the Act which pertain to SCCP wastes include hazardous waste, sludge, and solid waste. Relevant sections of these definitions include:

- hazardous waste -- "a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may ... pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed or otherwise managed." (23)

- solid -- "any solid, semi-solid, or liquid waste generated from an ... air pollution control facility ..." (23)

- solid waste -- "any garbage, refuse, sludge from an ... air pollution control facility ... including solid, liquid, semi-solid, or contained gaseous material ..." (23)

Any waste that is not discharged under a Section 402 New Performance Discharge Effluent Standard permit is considered a solid waste under RCRA. Metal cleaning wastes would be a solid waste when disposed of in landfills and an effluent when discharged under NPDES requirements.

9.1.3 Clean Air Amendments of 1977

Amendments to the Clean Air Act were enacted in August, 1977, setting out extensive pollution control rules which differentiate between regions with air not meeting national standards ("non-attainment areas"), and regions with air cleaner than national standards require. "Clean air" regions are divided into three "classes" of air quality according to the degree of purity desired for them, with the most stringent pollution limitations reserved for "Class I" areas, such as national parks, and the least stringent limitations applicable to "Class III" areas, where substantial industrial development is to be permitted. "Class II" areas are those where moderate development is desired.

The Environment Protection Agency has proposed regulations to implement the policy of preventing "significant deterioration" of air quality in clean air areas as required by the Act. The EPA proposals were published for public comment in November and December 1977, with final promulgation an ongoing process.

In addition, EPA promulgated immediately effective regulations for certain provisions of the Act, as required by Section 168. These include: (1) a listing of mandatory Class I areas; (2) the sulfur dioxide and particulate matter "increments" (additional pollution allowed beyond existing pollution) for all classes; (3) the new statutory definition of "baseline" (already existing) pollutant concentrations; (4) the exclusion of some areas from consideration for Class III classification (24).

EPA also proposed to accelerate implementation of other "PSD" (Prevention of Significant Deterioration) sections to make them effective on March 1, 1978. These regulations are not in effect. Under accelerated implementation, a number of new SCCP projects would fall under the new "best available control technology" (scrubber) requirements which had expected to be able to comply with low-sulfur coal under EPA's old, less stringent PSD rules.

9.1.4 Revised New Source Performance Standards

The Environmental Protection Agency proposed New Source Performance Standards (NSPS) in March, 1978, sharply limiting sulfur dioxide, particulate, and nitrogen oxide emissions from steam electric generating plants.

New Source Performance Standards are based on Section III of the Clean Air Act, which requires direct Federal emissions limitations for new, modified, or reconstructed pollution sources. A 1976 Sierra Club and Navaho Tribe petition for revision of the existing standards argued that technology advances since 1971 call for stricter standards.

According to the recently revised NSPS (25), the new standards would be: (1) for sulfur dioxide emissions, 1.2 lbs per million Btu and an across-the-board requirement for 90% emission reductions unless emissions are less than 0.6 lbs per million Btu. Reduction by 70% would be required below 0.6 lbs per million Btu. (2) For particulates, .03 pounds per million Btu; this emission level is based on the controls achievable, EPA claims, with electrostatic precipitators and baghouses. (3) For NO_x, the emission limitations would be fuel specific, as follows:

Bituminous coals, certain lignites, other solid fuels	0.6 lbs/10^6 Btu
N.D., S.D., Mont. lignite fired by a slag tap furnace	0.8 lbs/10^6 Btu
Gaseous fuels (except low-Btu synthetics)	0.2 lbs/10^6 Btu
Liquid fuels	0.3 lbs/10^6 Btu
Subbituminous coals	0.5 lbs/10^6 Btu
Low-Btu synthetic gas	0.5 lbs/10^6 Btu

While none of these new regulations apply specifically to trace elements, there is a relationship between trace element emissions and particulate emissions; (See Sections 4 and 5 of this report). In the present regulatory climate, particle control is the primary form of trace element control.

9.2 STATE ROLE IN COMPLIANCE WITH FEDERAL ENVIRONMENTAL REGULATIONS

9.2.1 State Implementation Plans

SIP's are important indirectly to the control of trace element emissions because these plans force the states to act to achieve primary ambient air standards. Primary ambient air standards contain a requirement for suspended particulate matter. There is a strong correlation to the level of suspended particles and trace element emissions (See Sections 4 and 5 of this report).

The SIP's continue to be amended to correct deficiencies found by the courts as well as to meet the technical changes required by emerging issues. The extent of approval of each SIP varies from state to state with no state plan currently fully approved.

On July 22, 1975, new procedures for the development, review, and approval of SIP revisions were initiated. These procedures will eliminate any distinction between "state initiated" and "EPA initiated" SIP revisions and will also eliminate the previous requirements for formal headquarters concurrence on most SIP approval/disapproval actions. The Regional Administrators now have authority to sign Federal Register notices proposing EPA-initiated SIP revisions in addition to their existing authority to sign such notices for state-initiated revisions.

The gap between the need for and availability of state and local air pollution control resources to attain and maintain ambient standards continues to exist. Additional state and local resources are needed to implement relatively untried or innovative control techniques, especially those pertaining to the siting of new sources and air pollution control programs that are related to land use and transportation.

9.2.2 Monitoring of Air Quality Maintenance Areas (AQMA)

Under the Clean Air Amendments, State Implementation Plans must include a thorough emission inventory (2). Such an inventory is one of the most essential ingredients of an air quality control program because it provides:

- input data for diffusion models,
- input data for cost-benefit analysis,
- data for the development of control strategies, and
- information for state and regional planning authorities.

Emission inventories are now routinely compiled by use of questionnaires, interviews, on-site inspections, and a number of published approximation techniques (26, 27). For easier comparison, the EPA prescribes further a specific format according to which the above information has to be presented (28).

Again the strong correlation between suspended particles and trace element concentrations should be remembered. Emission inventories can be used to obtain data for determining particulate emissions from point sources. If a trace element emission regulation should be promulgated, emission inventories will be one part of a suitable framework for enforcement of Federal regulations.

9.2.3 Effect of Permitting for New Source Performance Standards (NSPS)

The permit framework now used for NSPS is very relevant if actual control of specific trace element emissions should arise. That is, this permit framework will be a convenient mechanism already in place to implement new controls on trace metal emissions.

The permit system is specifically intended as a systematic means of not only achieving mass compliance, but, just as important, preventing the future growth in contaminant emissions. The permit system is a method which accounts for all factors (e.g., design, operation, maintenance, and administration) that must be considered in controlling any given source of air pollution (29,30).

The permit system provides for review of plans for construction, modification or operation of stationary source equipment or processes that have the potential to emit air contaminants. An application for a permit from an owner is required in advance of construction or operation of the equipment or process. The application provides the information necessary to evaluate the potential emissions from the equipment. Permits (or certificates) to construct or to operate are issued if, after thorough evaluation, inspection and source testing, it can be demonstrated that emissions will meet the standards of the agency throughout anticipated ranges and conditions of equipment operation. In some instances, permits are conditioned to assure that certain operational and maintenance practices are adhered to in the routine operation of the equipment.

The distinguishing features of permit systems are: (1) the authority such systems have over the construction and operation of all equipment capable of emitting air contaminants is clearly defined; (2) the clarity and specifics of the standards that must be complied with the procedures that owners must follow in submitting applications; and (3) the amount and type of technical information that must be supplied by the owner of affected equipment to permit source evaluation and to assure compliance with regulations (31, 32).

9.3 IMPACT OF ENVIRONMENTAL REGULATION ON SCCP's

9.3.1 Engineering Studies

A number of engineering studies have been done in response to environmental regulations promulgated for SCCP's. The Environmental Protection Agency (EPA) is preparing to establish a long-range schedule for promulgating New Source Performance Standards (NSPS). In order for future NSPS to be most effective, an overall strategy or plan of action is being developed so that priorities for standard setting can be established (33). A program to calculate the impact of NSPS on air pollutant emissions from industry within the United States has been developed. These calculations are performed using a generalized priority rating system known as Model IV (33) which mathematically expresses the differentials in atmospheric emissions that could be expected with and without NSPS.

Several other important engineering studies have been performed (34-37). One evaluation made by Jordan et al. (34) gives a review of the environmental impact of the entire process of fossil energy production from exploration to consumption. A focus is made on the specific industries for coal, oil and gas and other hydrocarbon sources followed by a review of public policies on much needed research.

In another study conducted by Bernstein et al. (35), an indepth investigation of the pollution from intermediate-sized boilers was carried out and consideration given to the possible methods of abating this pollution. This category of boilers includes all units used in commercial buildings, virtually all industrial units and some of the smaller utility-size equipment. All fossil-fuels were included. All commercially feasible means of controlling emissions were explored with respect to their efficiency, capital cost requirements and operating costs; this includes fuel switching, flue gas cleaning or treatment, combustion additives, and combustion design techniques. Because these boilers are small, often unattended, located in limited space and operated at low annual capacity, fuel switching is the most effective control strategy, especially as it will substantially reduce particulates and sulfur oxides. The four types of particle control equipment considered were dry cyclones, wet scrubbers, electrostatic precipitators and fabric filters.

A study done by Reiquam et al. (37) reported that certain control technologies aimed at achieving specific limits generate new waste streams which, in turn, require controls. Without a systematic assessment of these impacts, there is a substantial risk that pollution control strategies for controlling pollution in one medium will cause problems in another medium. For example, control of air emissions from coal-fired power stations will probably have impacts upon other media (land and water) when controls are imposed on the one medium (air). A complex methodology for assessing the impact of specific control technologies or strategies has been developed by Reiquam, et al (37). The assessment methodology consists essentially of evaluating an index for each control strategy and comparing it to a corresponding index for the uncontrolled case. The index is a function of the rate of production of pollutants, behavior of these pollutants in the environment, and relative importance of each pollutant. The cross media concept somewhat parallels the relationship between trace metals and particles since particle control impacts trace metal emissions.

9.3.2 Technology Advances

Some useful studies have been performed evaluating technologies that have developed due to response of environmental regulations (38-49).

In a study issued by Franklin Institute Research Labs (38), a survey of literature on control technology and regulatory aspects of sulfur oxide (SO_x), nitrogen oxides (NO_x) and particulate emissions from large, coal-fired boilers (chiefly utility boilers) was presented. In a report by Dr. J. L. Shapiro (40) current power generation technology is reviewed. In another study (41) models developed at Carnegie-Mellon University to systematically address tradeoffs between energy and environmental impacts in the context of conventional and advanced technologies producing electricity from coal are described.

9.3.3 Instrumentation Advances

Monitoring equipment to study and identify specific pollutants is a rapidly evolving technology. Trends in instrumentation are away from many older techniques using intermittant sampling or quick-sniff, grab samples. Even the continuous analyzer using chemical techniques are being nudged out by more advanced analyzers using physical measurement techniques (43).

9.3.4 Estimated Cost to Achieve Environmental Goals

The estimated cost to achieve environmental goals varies with the source of the estimate (48). The Ford Foundation Energy Policy Project, a two year study, projected the best way to achieve environmental goals is through conservation of resources. This would result in saving $300 billion in capital investments for energy producing facilities in the next 25 years (48). Also, an older TVA environmental cost analysis may still be informative (49).

9.4 STATUS OF ENVIRONMENTAL COMPLIANCE

9.4.1 Evaluation of Compliance to 1977

Long-term progress (1970-1976) can be seen in achieving compliance with the National Ambient Air Quality Standards (NAAQS) for total suspended particulate, sulfur dioxide, and carbon monoxide nationally and for photochemical oxidants in California. In the short-term, however, some reversals have taken place for total suspended particles with many areas experiencing increases between 1975 and 1976. Where photochemical oxidants are measured outside California, the trend appears basically stable over the 1973-1976 period. Nitrogen dioxide trends are stable in California; nationally, however, nitrogen dioxide levels tend to be increasing based mostly on three years of data. There are still insufficient data, however, to draw any definite conclusions on nitrogen dioxide levels outside California (34).

Air quality progress is measured by comparing the ambient air pollution levels with appropriate primary and secondary NAAQS for each of the pollutants. Primary standards protect the public health, and secondary standards protect the public welfare as measured by effects of pollution on vegetation, material, and visibility. The standards are further categorized for long- or short-term exposure. Long-term standards specify an annual mean that may not be exceeded; short-term standards specify upper limit values for 1-, 3-, 8-, or 24-hour averages that may not be exceeded more than once per year (50, 51).

The major findings of these investigations which pertain to particulate matter (and therefore trace metals) are as follows: (52-54)

- The general long-term improvement in total suspended particulate reversed itself between 1975 and 1976 with many areas experiencing increases. The likely explanation for this phenomenon is meteorological. Large areas of the country experienced drought during 1976. These extremely dry soil conditions increased the likelihood of wind-blown dust contributing to ambient particulate levels.

- A major decrease was observed in the population exposed to high particulate levels in Metropolitan New York, Chicago, and Denver. The greatest improvement occurred in the New York-New Jersey-Connecticut Air Quality Control Region, where

> the percentage of the population exposed to particulate levels above the annual primary health standard decreased from 60 percent in 1970 to 0 percent in 1976. Similarly, Chicago decreased from 100 percent in 1970 to 64 percent in 1976; Denver decreased from 83 percent in 1970 to 74 percent in 1975.

9.4.2 Recent Regulatory Trends

The state of New Mexico now has in effect a recently passed regulation on emission of particles from coal burning power plants (55). The regulation as written allows a maximum particulate emission of 0.05 lbs per million Btu. More importantly, a limit of 0.02 lbs per million Btu is set forth for particles with a mass median diameter less than two microns. Elsewhere in this report (See Sections 4 and 5) it has been shown that some trace metals may be enriched on particles less than two microns emitted from coal combustion processes.

It is important to note that this regulation is part of the state of New Mexico SIP's. It would therefore appear that regulatory acts already in effect can be further utilized to start regulation of trace metal emissions (See Sections 9.2 and 9.3 of this report). The strong correlation between fine particulate emissions and trace metal emissions may be one way to indirectly control trace metal emissions without an additional statute that limits trace metal emissions specifically. The reader should be cautioned that further study into particle and trace metal emissions and correlations must be done before such actions would be justifiable.

Just recently (October, 1978) lead has been made a criteria pollutant. The National Ambient Air Quality Standard (NAAQS) is 1.6 $\mu g/m^3$ averaged over a three month period. SIP's for control of lead emissions were due as of July 1979. Full attainment is scheduled for October 1982 (56).

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SECTION 10

FUTURE RESEARCH

One of the objectives of this project was to identify areas where research is needed. These needs are of two general types: one is merely filling in gaps in the data, while the other need is for innovative, creative research on problems of current and future interest. New analytical techniques and instrumentation dictate in part the feasibility and practicality of meeting some of these needs. Specifically for trace metals, the recent availability of simultaneous, multi-element analytical techniques, such as ICAP (Inductively Coupled Argon Plasma) should greatly facilitate (in cost, time, and number of samples) the investigation of trace metals in all types of materials. For greatest accuracy INAA (Instrumental Neutron Activation Analysis) is probably the preferred technique because no sample pretreatment is required (see Section 8).

The directions in which technological research will be steered are influenced by predictions of potential future problems. These scenarios, coupled with a knowledge of current research, data, and available technology, will be used to determine funding priorities. The Accuracy of Data section of this report (Section 8) reviews current trace metal detection technology and what is expected in the near future. At the end of each major section is a subsection discussing the research needs specifically applicable to that area. A summary of those subsections should reasonably well serve to identify data gaps and areas for further research related to those fields. This section will deal more with sources of current information and broad-based, interdisciplinary research needs identified in the literature.

10.1 SOURCES OF INFORMATION

To properly evaluate future research needs, one must first identify all recent and current research in the field of concern. With the advent of computerized bibliographic, statistical, granting and funding databases, information is more readily available from a potpourri of database vendors; prominent among them are:

- ORBIT -- Systems Development Corporation,
- DIALOG -- Lockheed Retrieval Services,
- MEDLARS -- National Library of Medicine,
- DOE/RECON -- U. S. Department of Energy, and
- STAR -- (Scientific and Technical Aerospace Reports) -- by National Aeronautics and Space Administration (available only to NASA contractors or in hard copy).

These services contain, in part, bibliographic references covering about 130 databases. Many entries include abstracts, all are keyworded, and many foreign entries are included. Most research libraries have access to one or more of these services. Included among the bibliographic databases covered are Government Reports Announcements (by NTIS, National Technical Information Services) and Chemcon (covering Chemical Abstracts). U.S. patents are also covered.

Granting and funding reports are covered by SSIE (Smithsonian Science Information Exchange), GRANTS (the Oryx Press, Phoenix, Arizona), and RIP (Energy Reports in Progress), TIC (Technical Information Center) at ORNL, (Oak Ridge, Tennessee). These reports contain summaries of research, either in progress or completed within the last two years, and cover the physical, social, engineering, and life sciences. Input is from over 1300 sources, governmental and private, but about 90% is generated by the Federal government and their funding. This service is designed to pick up most ongoing federally supported research. All of the above-mentioned databases are included in ORBIT and DIALOG; MEDLARS refers to the medical literature.

Government Reports Announcements is a monthly NTIS publication (Springfield, Virginia) which abstracts all Federally sponsored research reports.

Most of the entries refer to final reports and extend back to 1964. The data from this publication are also included in the NTIS computerized database. Monthly Catalogue, a USGPO (Washington, D.C.) publication, contains information about most finalized research projects which were Federally conducted. These data have been on-line since 1976.

STAR would be useful for ambient atmospheric data but it is not on-line and is available only to NASA contractors. A hard copy is available to anyone. GRANTS covers references to grants offered by federal, state, and local government, commercial organizations and associations and private foundations covering 88 academic disciplines. RIP has been developed at ORNL in cooperation with the Energy Research and Development Inventory Project of ORNL. The research, development or demonstration projects covered include all types of funding, and the scope of interest includes all energy sources (fossil, nuclear, unconventional), electric power (generation, transmission, distribution, storage), energy conservation and utilization (heating, cooling, lighting, transportation, etc.), economic and legal aspects, health and environmental effects, basic and applied research and engineering development, and more.

Such services described above should enable anyone with a research library access to identify with key word accuracy essentially all data or research published up until about six months prior (the lag time for publications being entered into the data base). Also, most ongoing research can be identified through granting records or interim reports.

There has not been a wholly successful effort to bring together all information on research of specific concern, however. Most private research laboratories (e.g., EPRI, Batelle, SRI, etc.) publish quarterly or yearly summaries of research and current projects. For completeness, each lab must be contacted individually. Also, each government agency generally publishes a summary of work funded under its aegis. Examples which are relevant to trace metal emissions from SCCP's include EPA (1, 2), DOE (30, and interagency publications (4, 5). But again for completeness, each agencies' publication(s) should be reviewed. Finally, of particular interest to this project is a Mitre report (6) reviewing current (July 1978) research projects involved with the CCEA program.

10.2 ANALYTICAL TECHNIQUES

The pace of advancing technology to some extent dictates the rate of research development. Until reliable, commercial atomic absorption spectrometers became available, extensive elemental determinations were difficult, expensive and required a highly trained operator. Before 1960, few elemental determinations were reported. As technology evolved in the 1960's, data on trace elemental studies became more common. But it was not until about 1970, when such determinations became reliable and more automated, that trace metal studies began to proliferate. With the data becoming more available, the scientific community was better able to define what problems existed and channel the funding of research to the most pressing problems. Little of the reliable trace metal information occurs in the databases before 1970; coincidentally, most of the computerized information retrieval systems began at about the same time.

Today, new developments in analytical instrumentation are ushering in a new era in trace metals research (7). Simultaneous multi-element determinations are becoming the standard method. Isotope dilution-mass spectrometry is now sufficiently accurate to provide reliable data. X-ray fluorescence is quick and relatively inexpensive and reasonably accurate. Neutron activation methods show a high degree of consistency between labs which suggests a high degree of accuracy (8). And plasma fluorescence has lowered the cost of a 35 element analysis below fifty dollars and instrument time to five minutes. See Section 8 for a review of techniques.

The conclusion is that trace metal analysis of most types of samples will become relatively easy and inexpensive. The number of trace element determinations will profliferate, and soon, the existing data gaps will be filled. Coal has received the most study among SCCP fuel alternatives, and rightly so owing to the pollution load per Btu compared with other fuels;

however, this project uncovered a relatively small amount of information on trace metal emissions from oil, gas, wood or municipal refuse fuel sources. Coal also accounts for nearly half the energy produced by electrical utilities. Only a few studies have been reported in the United States on trace metal emissions from package boilers (small, self-contained units) and from residential combustion. With trace metal analysis becoming faster and cheaper, many heretofore neglected sources will be more amenable to analysis. Included among these are other types of incinerators (pathological, industrial, waste disposal), fireplaces, open burning, etc.

Other techniques are beginning to attack the problem of chemical speciation -- that is, determining the molecular form of the trace metal under study. Raman (19), auger (10), photoelectron (11), and photoacoustic spectroscopy (12) are being used or considered for the study of chemical species on fly ash or ash-type particles. In the near future, as analytical techniques improve and awareness of the problems they can solve evolves, information about the molecular form of trace metals from combustion sources will grow.

Also, with trace metal analysis more available, increased efforts will very likely be directed at emissions from process heating (heat used in industrial processes). While this type of combustion is not strictly a SCCP source, in many regions it accounts for a considerable fraction of the heat produced and more than its share of pollutants, especially trace metal pollutants. As an understanding of trace metal emissions and their environmental fate develops, more attention will have to be paid to industry sources outside of the utility sector.

10.3 ALTERNATE FUELS

Fossil fuels make up the vast majority of combustion fuels today. While this situation is not expected to change in the foreseeable future, there will likely be a shift within the fossil fuel regime in the United States towards more coal and coal by-products (liquefaction, gasification, in-situ combustion, etc.) and possibly oil shale; generally, however, these nonconventional processes are not commercially available at this time and do not fall under the definition of an SCCP.

Many studies predict the increased utilization of coal in the United States (for example, see 13). While most speculate on the future particulate load, few explicitly mention the parallel increased trace metal emissions problem. Literature dealing only with particulate matter was not picked up in this search unless trace metals were mentioned. However, the increase in coal use implies a concomitant increase in the mobilization of trace metals through the burning of coal. Control technologies (Section 4) and regulations (Section 9) will simultaneously evolve and influence one another. Thus, regulations and technologies directed at particle control will have an impact on trace metal emissions as well. Anyone concerned about trace metal pollution will therefore have to keep abreast of the status of particle control.

Walker _et_ _al_. (14) are interested in the catalytic conversion of coal to more useful fuels, processes which they claim will become even more important. They report that it will be justifiable, indeed necessary, to spend large sums of money learning to characterize coal. Their particular concern is that trace metals play an important part in catalysis considerations, and far too little is now know about the role of these trace metals in catalysis.

There are two candidates for non-fossil fuels that could make small inroads into the nation's energy mix. The burning of municipal refuse, often augmented by fossil fuels, is seen as a simultaneous solution to the disposal of the burgeoning volume of trash and a novel, albeit small, fuel source (15). Municipal refuse is much lower in sulfur than coal and somewhat higher in chlorine; mixing of the two fuels will dilute the emissions per BTU for both. An assessment of the trace metal content of refuse was presented in Section 3.2, however, the emissions "resulting from the thermal conversion of waste-to-energy are somewhat unknown." (16) Particulate emissions are the most apparent problem, but cadmium, copper, iron, lead and zinc have also been identified in the flue gas and fly ash; see Section 5.7. Devitt _et_ _al_. (16) also discuss the state-of-the-art (1978) control technologies available for urban refuse, power generation boilers. Also, the need for research into boiler types designed for refuse-generated power has been indicated by Schwieger (17).

Wood has also been proposed as a possibly significant fuel in the future. However, only a few reports were identified in this study that dealt with trace metals and wood (18). The trace metal content of paper products, often due largely to the printing inks upon them, has been analyzed and was presented in Table 3-11. In summary, the two possible alternate fuel sources, trash and wood, remain largely unstudied as fuel sources with regard to trace metals.

10.4 HEALTH AND ENVIRONMENTAL EFFECTS

The complete review of the health and environmental effects from trace metals from SCCP is found in Section 6 of this report. Included at the end of that section is an assessment of research needs, particularly those designed to fill data gaps. However, several papers specifically refer to research needs, and those are reviewed here.

The primary area of concern is the unknown chronic effects, both occupational and public, attendant with the increased use of coal. Gibson (19) has reported that safe exposure levels of hazardous substances from coal combustion are mostly unknown; he urges toxocological studies as well as monitoring and gathering more control data. Comar, et al. (20) discuss the nature and measurement of health effects from energy production. Exposure-response relationships, risks of death and health effects are considered for all modes of energy production; coal is the most hazardous means of energy production. But they conclude, "all data are, however, uncertain, and massive research is needed." McBride, et al. (21) have cautioned to include consideration of the total cost, monitary and environmental, of energy, mining to emissions, in any comparison of available types of energy.

Wittenberger (22), recognizing the increased health hazards of coal-generated power, has also warned that the health costs of the conversion to coal should be factored into any total assessment. Since chronic effects are largely unknown, such factors need to be determined. Comar and Nelson (23) reported the results of a workshop that considered future energy needs and the effects of fossil fuel combustion products on human health and well-being.

Again, the conclusion is that not enough is known about the health effects to accurately assess the magnitude of the problem and to pinpoint the areas of acute concern. Ermak et al. (24) also recommend a comprehensive assessment for future power production in the Southwest, but noted that the paucity of relevant data make such assessments unreliable.

Finally, a paper from Argonne National Labs (25) recommends a balanced research program into the biomedical and environmental effects of coal extraction, processing and combustion. Further, that research should be integrated across all energy technologies to more capably direct and control the energy mix in the future. They judged it necessary to group research projects into broad program units (which they list) with objectives, scopes, milestones and costs.

While all these authors are dealing with the general need for more health and environmental data on coal combustion, none specifically mention trace metals. Yet all are concerned with the total pollution problem, and many of the trace metal difficulties have not even been identified well enough to be factored into the scenarios; however, all the papers, implicitly or indirectly, relate to the trace metal health problem.

10.5 TECHNOLOGY ASSESSMENT

Closely related to health and environmental assessment and the indicated research needs, is the area of energy technology assessment. That is, studies which are trying to predict the energy picture for the future are often ultimately directed at the health impact; however, such predictions involve many guesses and estimations as input parameters, and the results are not usually specific. Essentially none of them get down to the level of trace metal pollution. The most popular method in assessment is to extrapolate current conditions against a demand axis to generate rough, "ball-park" predictions of combustion and emission levels. For example, several publications by the Interagency Task Force on Energy/Environment Research and Development programs which this study reviewed (26, 67) failed to specifically mention trace metal pollution. They are concerned with particles and total pollution loading from all potential energy sources and control technologies, but any trace metal predictions would be possible only by inference. Other reports, typical of the discipline, reflect the same level of predictive uncertainty (28-30). A recent book by Kash et al. (31) on the role of research, development and demonstration in the nation's energy future fails to even mention trace metals in the index. Rather than reflecting on any author or study, the lack of specific consideration of the trace metal emissions in the future simply reflects the state-of-the-arts of pollution knowledge and assessment or prediction.

One study, which is specifically attempting to assess trace metal body burdens that would result from increased coal utilization, was recently reported by Gasper and Dauzvardia (32). They assume current levels of pollution will increase proportionally with increased power demand and coal use in the Illinois River Basin. They conclude that by the hypothetical year of 2020 that trace metal body burdens will be about doubled.

Reiquam et al. (33) have warned that improved control technologies can no more than transfer the pollution burden to another wastestream. Indeed, controlling pollution in one medium will increase the severity of problems in another. They present a methodology for assessing the cross-media impact of specific control technologies and predicting the net effect of a particular strategy on the environment. The methodology is demonstrated for a 1000 MW coal-fired power plant. The energy consumption, capital costs and operating costs are also considered.

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GLOSSARY

AAQS: Ambient Air Quality Standards (Federal)

ACFM: Actual Cubic Feet per Minute

AEC: Atomic Energy Commission

AEROS: Atmospheric and Emissions Reporting System

Aerosol: Fine particles (solid or liquid) suspended in a gas.

Ames Test: A short-term, in-vitro test for mutagenicity (DNA damage) involving the reversion of a histadine requiring strain of bacterium (Salmonella typhimurium) induced by a chemical agent.

Anthropogenic: Being caused or generated by man.

AQCR: Air Quality Control Region

BET: A method developed by Brunauer, Emmett, and Teller, to measure the surface area of small particles by monitoring the adsorption of a gas, assuming a monolayer; commercially available.

BTU: British Thermal Unit, equivalent to 1055.1 Joules.

CAMP: Continuous Air Monitoring Program

carcinogen: An agent that can cause cancer.

CCEA: Conventional Combustion Environmental Assessment (an EPA Program).

CFR: Code of Federal Regulations

Chalcophile: A mineralogical class of elements that are frequently found as sulfides.

Curie: A unit of radioactivity equal to 3.7×10^{10} disintegrations per second.

EPC: Estimated Permissible Concentration (a safe environmental level of a pollutant).

ESP: Electrostatic Precipitator (a device designed to remove particles from a gaseous stream).

Fly ash: The solid particles resulting from the combustion of a fuel that are entrained in the flue gas; sometimes meaning only the particles that leave the process via the stack emissions.

ICRP: International Commission on Radiological Protection

IERL: Industrial Environmental Research Laboratory (EPA)

INAA: Instrumental Neutron Activation Analysis

LC-50: Lethal concentration; the concentration which causes fifty percent mortality in a population

LD-50: Lethal Dosage; the dosage which causes fifty percent mortality.

Lithophile: A mineralogical classification for those elements frequently found combined with oxygen (or frequently silicon dioxide).

MATE: Minimum Acute Toxicity Effluent; the minimum concentration in an effluent that is believed to be acutely harmful.

MEG: Multimedia Environmental Goals

Micron: Common contraction of micrometer.

MMAD: Mass Mean Aerodynamic Diameter

NADB: National Aerometric Data Bank

NADIS: National Aerometric Data Information Service

NASN: National Air Sampling Network

NIOSH: National Institute for Occupational Safety and Health

NRC: Nuclear Regulatory Commission

Non-metal: Those elements in the upper right portion of the periodic table having no metallic properties (H, C, N, O, F, P, S, Cl, Br, inert gases).

NSPS: New Source Performance Standards

NTIS: National Technical Information Service

Oncogenic: Tending to cause tumors.

ORNL: Oak Ridge National Laboratory

ppm: Parts per million

PSD: Prevention of Significant Deterioration, or Particle Size Distribution

RCRA: Resource Conservation and Recovery Act (1976)

REM: A dosage of radiation that will cause the same biological effect as one Roentgen of X-radation.

RTP: Research Triangle Park: an EPA/IERL

SAROAD: Storage and Retrieval of Aerometric Data

SCCP: Stational Conventional Combustion Process

Semi-metal: Those elements which exhibit some metallic characteristics, but not all; B, Si, As, Se, Te, I, At

SIP: State Implementation Plan

SRM: Standard Reference Material; a series of representative, quantified reference materials available through National Bureau of Standards

Synergism: The interaction of two entities to produce an effect different than merely the sum of their independent effects.

Teratogen: An agent that can cause fetal changes and birth defects.

TLV: Threshold Limit Value; refers to the maximum presumed safe level for ambient concentrations; given in MEG's.

Trace element: those elements which are found in concentrations less than 0.01 percent (100 ppm); not a sharp definition.

TSP: Total Suspended Particulate

TVA: Tennessee Valley Authority

WHO/FAO: World Health Organization/Food and Agricultural Organization